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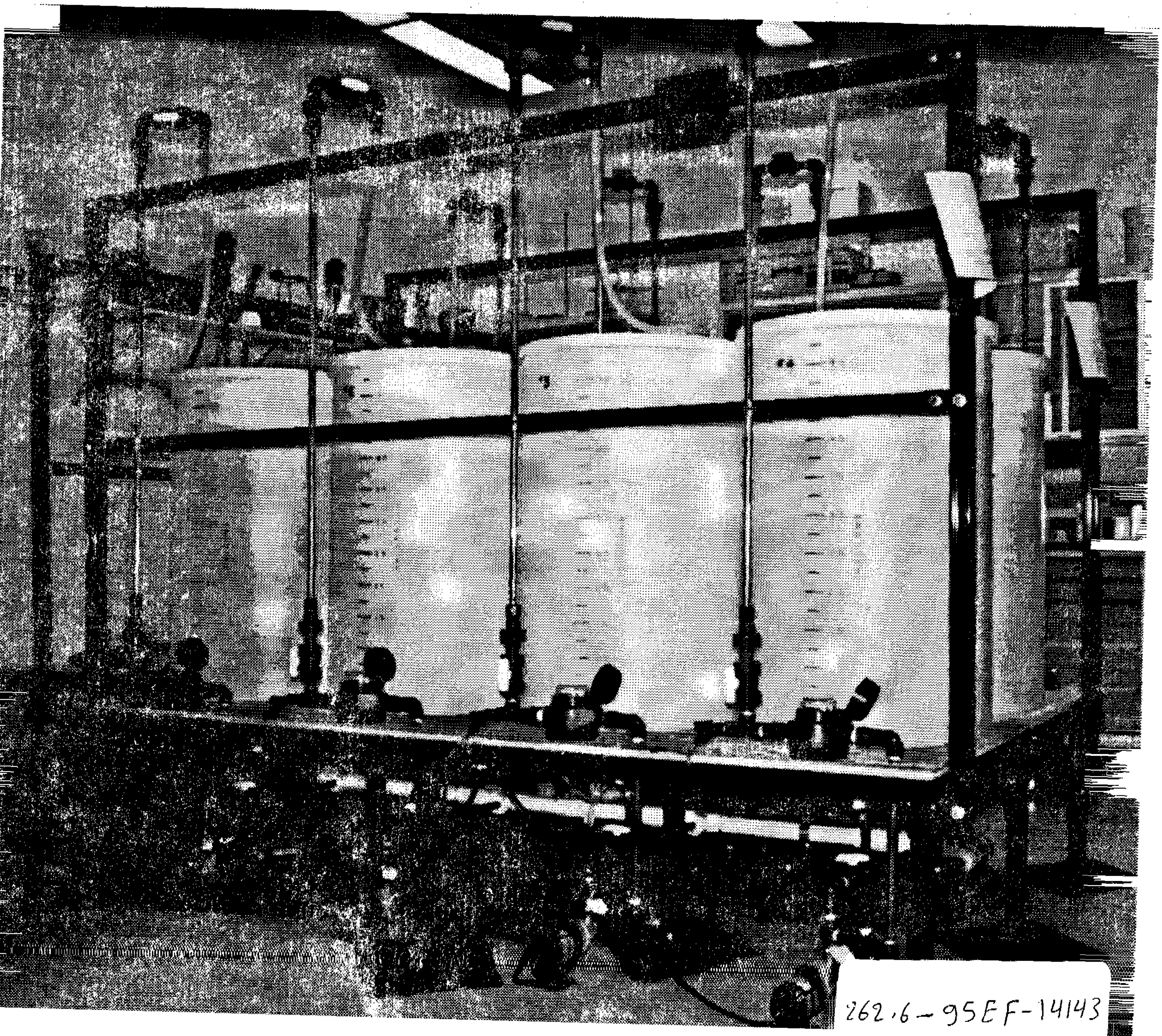
# Effect of pH, DIC, Orthophosphate and Sulfate on Drinking Water Cuprosolvency



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# Effect of pH, DIC, Orthophosphate and Sulfate on Drinking Water Cuprosolvency

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E. Timothy Oppelt, Director
National Risk Management Research Laboratory

# Abstract

Field data from various copper monitoring studies and Lead and Copper Rule compliance data are often inappropriate and misleading for reliably determining fundamental chemical relationships behind copper corrosion control. To address this deficiency, a comprehensive solubility model for copper in drinking water has been developed, that is qualitatively and quantitatively consistent with available data for copper dissolution and precipitation. The concentration of Cu(I) is dominated by $Cu_2O(s)$ or CuOH(s) solid phases, plus soluble aqueous ammonia and chloride complexes. For young piping, the concentration of Cu(II) is mainly governed by $Cu(OH)_2(s)$ (cupric hydroxide), rather than CuO(s) (tenorite) or $Cu_2(OH)_2CO_3(s)$(malachite). Complexation of Cu(II) by DIC and hydroxide ion is extremely important. Increases in DIC are predicted to cause significant increases in copper solubility in the pH range of 7 to 10. Often, utilities must trade off increasing cuprosolvency by DIC addition for ensuring adequate buffering intensity in the finished water. Sufficient dosages of orthophosphate in the pH range of 6.5 to 7.5 may reduce cuprosolvency, while sulfate may assist in controlling cuprosolvency under some chemical conditions, or may interfere with the formation of cupric hydroxide films under mildly alkaline conditions. Dissolved oxygen and chlorine residual play complicated roles in determining copper concentrations after various standing times. Frequently, 48 to 72 hours are necessary to reach equilibrium levels of copper in disinfected systems. Considerable uncertainties in much of the important thermodynamic data for copper species still exist, and many research needs remain that are critical to improving the understanding and control of cuprosolvency. This report covers a period from June 1993 to November 1993, and work was completed as of (date).

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# Acknowledgments

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# Introduction

The promulgation of the "Lead and Copper Rule" by the USEPA in 1991 has required approximately 80,000 water utilities nationwide to monitor for copper resulting mostly from the uniform corrosion of copper plumbing materials.[1-4] A complete breakdown of monitoring results covering lead and copper levels and associated water quality parameters for the first two rounds of sampling by all utilities has not been verified and made available for analysis. Therefore, the exact extent of the problem is hard to quantify. However, in the first round of monitoring by the large water systems (about 682), approximately 6 % exceeded the 1.3 mg/L action level according to a recent study.[5] Examination of data from 7,600 medium- and large-sized utilities entered into the Federal Reporting Data System (FRDS) indicated the largest relative fractions of utilities reporting exceedence of the action level were generally in the Northeast and Pacific Northwest regions of the country.[4] However, the highest relative fraction overall occurred in Nebraska (49%), and the states of Minnesota (21%) and Iowa (16%) also had high copper levels in a relatively large fraction of water systems of these sizes. The highest copper levels in the water for locations served by large utilities appeared to be in the Southeastern and Western regions of the United States, in utilities covering a considerable range of water qualities.[5] Generally, the action level was exceeded more frequently in water systems having ground water sources.[4]

The cuprosolvency (copper solubility) problem apparently increases with decreasing utility size. For example, on the basis of data from the USEPA Office of Ground Water and Drinking Water and two other reports are that for medium-sized systems in their first round of sampling, the action level was exceeded by 87 utilities in Massachusetts, 57 in Florida, 32 in New York and Illinois, 27 in Pennsylvania and Washington, and 26 in Minnesota.[6,7] In the first round of regulatory monitoring, approximately 485 medium-sized utilities exceeded the copper action level according to these sources. For both rounds, a total of 600 of 7600 utilities exceeded the copper action level.[4]

Unfortunately, the regulatory monitoring data are of limited use for extracting details of copper chemistry behavior and understanding potential copper passivation strategies. Several important problems with such an approach are the following.

- Water quality parameter data are required only from utilities not meeting the Lead and Copper Rule Action Levels, so the information is not reported or even not collected by many utilities.[1-3,8]

- For medium-sized water systems, water quality parameter data were frequently, collected at different times than the samples for lead and copper. In practice, many utilitites first collected the source water and first-draw water samples, to see if they met the 90th-percentile action levels for lead and copper. If they found they were below the action level, reporting of such data was not required. Hence, it was often not collected. If they were above the action level, they collected the water quality data.

- Water quality data does not necessarily represent values at the initiation of water stagnation for regulatory sampling. Geographic (within the system) location and synchronization of water chemistry characterization with lead and copper levels is critically important to assess chemical relationships behind corrosivity and treatment options. Without employing these important sampling principles, making a direct statistical or mechanistic link between background water chemistry conditions and the corresponding lead and copper values becomes numerically possible but scientifically meaningless. Therefore, using existing regulatory data for such comparisons is only valid for systems having extremely consistent water qualities over time, and throughout the distribution network.

- Data regarding some important background chemical constituents that might influence copper corrosion (eg. chloride, sulfate, silica, orthophosphate, etc.) are not necessarily collected, particularly when corrosion inhibitors (phosphates, silicates) are not employed.

- Stagnation times of monitoring samples are permitted to fall within a ten-hour period (6-16 hours). Considerable scatter in tap water data resulting from differences in standing time have been observed by Wagner.[9]

- Copper dissolution rates depend greatly on the age of the passivating films, so interpretation of monitoring data must include adjustment for various plumbing ages to correctly deduce differences in cuprosolvency resulting from chemical rather than temporal factors.

- Surface films remaining on the interior pipe surface from the manufacturing process can affect passivating films formed in the plumbing systems.[10] The persistence and impact of these films on subsequent copper dissolution into the water will depend greatly on the entire usage pattern of the individual plumbing system.

- Lead and copper monitoring sites are purposely biased to represent locations tending to contain high levels of lead, such as sites with lead interior plumbing, lead service lines, and high-lead solder installed after 1982.[2] Consequently, in many cases the collected sample volume may not have been exposed to copper plumbing.

- High copper levels that could considerably exceed the new 90th-percentile U. S. action level may go undetected in the regulatory monitoring process. For copper, the highest corrosion rates and solubilities will most often be associated with the newest piping. These sites will normally be outside of the priority monitoring site tiers, leading to the interesting possibility that a water supplier may pass the regulatory action level requirement, but may still have a copper solubility problem.

Nonetheless, several interesting gross-scale trends have been discerned for large water systems.[4,5] There is a poor correlation between 90th-percentile lead and copper levels. Another trend is that copper exceedences tended to be highest at very low alkalinities (<25 mg $CaCO_3$/L) and increasingly greater over 75 mg $CaCO_3$/L. Finally, no action level exceedences were reported for systems having a pH above approximately 8.

The data thus far suggest that cuprosolvency will be a major concern across the United States, especially for smaller water suppliers that are less likely to employ corrosion control and use ground water sources. Further, the poor correlation between reported 90th-percentile lead and copper levels suggests that different control strategies for copper than those considered appropriate for lead may need to be developed or employed by affected utilities. Understanding how copper will respond to lead control measures and the results of other regulatory treatment requirements is therefore of considerable interest. Indeed, a response that effectively controls lead corrosion might exacerbate copper corrosion. Moreover, a utility must distribute aesthetically-pleasing water. A good example of the conflicts between control of corrosion of iron mains and reducing copper corrosion rates has been given for a study in Vancouver, BC.[11]

## Historical Framework

While many previous papers and book sections have been published concerning copper corrosion, the focuses of most were on unusual corrosion phenomena or pitting. A summary of considerable copper corrosion literature has been developed by Cruse and von Franquè.[12]

A review of the general literature on copper chemistry in drinking water and natural water systems led to the conclusion that the basic cupric hydroxy-carbonate compound $Cu_2(OH)_2CO_3$ (malachite) should form a passivating film over the pipe surfaces in many water systems, and reduce the corrosion potential. The fact that many utilities reported soluble copper levels that far exceeded predictions based on malachite solubility raised important questions about the accuracy of this assumption.

The great influence of pH on copper corrosion has been widely accepted. Attack on copper by "dissolved $CO_2$" or "carbonic acid" has been reported by many investigators, although the mechanism has been a matter of some debate.[12,13] However, much confusion still exists in the drinking water treatment field about what constitutes a corrosive water toward copper plumbing materials.

The confounding nature of the many variables impacting metal solubilities and leaching rates makes comparing a large number of possible treatments a cumbersome and daunting task for individual utilities considering experimental evaluations. It also obscures basic interrelationships, by compounding intrinsic chemical variability and impacts with artifacts caused by even subtle differences in experimental testing protocols.

In attempting to address some of the data gaps for cuprosolvency control by utilities, a variety of experimental systems have been constructed and operated in USEPA laboratories. During these experiments, some perplexing data was generated that appeared to either contradict some "conventional wisdom" on copper corrosion, or showed unexpected sensitivities to important water chemistry variables and experimental system operational protocols. These observations provided the initial motivation to begin exploring the copper solubility issue in detail.

If an accurate equilibrium model for cuprosolvency were developed, it would provide utilities and consultants with a practical tool for selecting and applying corrosion control programs that will work over the long term. A sound theoretical and practical understanding of the important factors affecting cuprosolvency would greatly obviate the need for what are often complicated, costly, and sometimes misleading bench-top and pilot-plant experimental studies. Small and medium-sized water systems frequently lack the technical sophistication, as well as the mechanical and financial resources, needed to conduct complicated demonstration studies. For water systems able to conduct experimental treatment evaluations, an accurate model for cuprosolvency would reduce the need for including fundamental tests (*eg.* pH and carbonate concentration effects) in their evaluations. Utilities could then concentrate on determining the need for additional experimental evaluations of inhibitor treatments or investigation of other unusual chemistry characteristics of particular water systems.

A better understanding of roles of pH and DIC (dissolved inorganic carbon) in cuprosolvency would greatly improve the accuracy of regulatory "desk-top" corrosion optimization evaluations, thereby providing a better assessment of long-term treatment impacts than those ascertained over a short time-frame (*ie.* weeks, months). Finally, an accurate solubility model for copper would allow many utilities to achieve the requirements of the Lead and Copper Rule without the need to conduct the treatment studies.

A newly-emerging indirect constraint on copper corrosion control in drinking water is by wastewater effluent guidelines and limits that are becoming increasingly stringent. Ironically, ambient corrosion of domestic, commercial and institutional plumbing systems is now becoming a "contaminant" of wastewater that is becoming difficult to control through normal waste treatment processes. The development of an accurate model for copper solubility will allow the evaluation of treatment alternatives for optimizing the control of cuprosolvency beyond drinking water regulatory requirements, to achieve adequate levels at the end of wastewater treatment.

## Study Objectives

This fundamental purpose of this initial phase of copper corrosion research was to tie together into a comprehensive solubility model various aspects of both the aqueous and solid speciation of copper under redox potential conditions typical of municipal drinking water systems. This model development and presentation would clarify the interrelationships among copper solubility, pH and the concentrations of various aqueous carbonate species in potable waters. The solubility model developed, which will subsequently in this paper be called the "cupric hydroxide model," provides a rational basis for applying pH and DIC adjustment for domestic plumbing corrosion control through central water treatment. Further, the model also provides an essential foundation for future research targeting the effects of other important solutes, such as chloride, sulfate, ammonia, chlorine species, and "natural organic matter" (NOM) on copper corrosion. The model also helps explain the reduction in cuprosolvency brought about by aeration of many ground water supplies for the removal of contaminants such as radon, VOC's, or iron.

To show at least initial evidence that the solubility model has promising practical validity, appropriate experimental data from various other corrosion investigations performed by the Drinking Water Research Division (DWRD) of the U.S. Environmental Protection Agency, and data collected by other investigators were re-evaluated in the framework of the new model. New laboratory experiments in copper solubility were initiated, and furure research by DWRD with these and other experimental systems will be used to further test the model and refine both the selection of critical aqueous and solid species to be incorporated into the model, and constraints on the applicability of the model to pipe loop corrosion tests and real water distribution systems covered by USEPA regulations.

# Copper Chemistry Overview—The Theory

## Thermodynamic Data Used for Modeling

Table 1 gives a listing of a selected set of internally-consistent Gibbs Free Energies of formation ( $\Delta G_f^\circ$) for copper and related chemical species, along with their origin. Equilibrium constants used in this work were computed for 25°C from $\Delta G_f^\circ$ values from this table by the standard technique.[14-16] Although some researchers have made predictions of copper corrosion behavior at elevated temperature[17], adequate information is generally not available to characterize equilibrium and solubility constants for many important copper compounds and complexes at temperatures other than 25°C. Data are particularly lacking for the carbonate complexes (that dominate cupric ion speciation above about pH 7), hydroxide solids, and phosphate species. Therefore, no attempts at such modeling are presented in this paper. Research on $Cu_2(OH)_2CO_3$ (malachite) solubility in sea water has indicated that the net effect on copper solubility may be a significant decrease at low temperature.[18-20] but differences between sea water and most drinking waters affects the speciation to a degree that quantitative extrapolation is unreliable. Part of the extrapolation problem results from decreases in the solubility constants of some important copper solids as temperature increases, analogous to the well-known case of calcium carbonate. However, the aqueous complexes that dominate copper speciation do not necessarily follow the same equilibrium constant trends with temperature as do the solids.

Computations of copper solubility in the following sections were made using a variety of software on IBM-compatible personal computers. The software used included Lotus 1-2-3®† (Release 3.1+) for copper(I) computations, and Microsoft FORTRAN 5.0†† for copper (II) system calculations. A FORTRAN computer program, CU2SOL, was written specifically to compute the solubility of copper(II), following the pattern previously established with LEADSOL.[16,21,22] Potential-pH diagrams ("Pourbaix" diagrams) were computed using a version of the WATFIV computer program of Froning, *et. al.*[23] modified for use on the personal computers with the FORTRAN 5.0 (DOS) compiler. Graphical output was produced either manually or by importing ASCII-format data files output from the PC programs or worksheet files from the spreadsheets. Graphing software used included Freelance Graphics for DOS®[†], SigmaPlot® for DOS and Windows[†††] (versions 5.01 and 2, respectively), PowerPoint®[††] version 3.0, and Surfer®[††††] for Windows packages. SigmaPlot® for Windows and Surfer® for Windows were used for interpolation of copper concentrations in the construction of solubility "contour" diagrams.

**TABLE 1. INTERNALLY-CONSISTENT GIBBS FREE ENERGIES OF FORMATION-COPPER AND RELATED SPECIES AT 25°C**

| Species | $\Delta G_f^\circ$kcal/mol | $\Delta G_f^\circ$kJ/mol | Reference |
|---|---|---|---|
| | Cu(I) Aqueous Species | | |
| $Cu^+$ | 11.95 | 49.98 | [1] |
| $CuCl^0$ | -23.12 | -96.72 | [2] |
| $CuCl_2^-$ | -58.29 | -243.89 | [3] |
| $CuCl_3^-$ | -88.76 | -371.35 | [3] |
| $Cu_2Cl_4^{2-}$ | -115.71 | -484.12 | [3] |
| $CuNH_3^+$ | -2.44 | -10.20 | [4] |
| $Cu(NH_3)_2^+$ | -15.46 | -64.67 | [4] |
| | Cu(I) Solid Species | | |
| Cu(OH) | -43.50 | -182.00 | [1] |
| $Cu_2O$ | -35.01 | -146.47 | [5] |
| | Cu(II) Aqueous Species | | |
| $Cu^{2+}$ | 15.65 | 65.48 | [1] |
| $Cu(OH)^+$ | -30.18 | -126.28 | [6] |
| $Cu(OH)_2^0$ | -75.57 | -316.21 | [6] |
| $Cu(OH)_3^-$ | -117.72 | -492.55 | [7] |
| $Cu(OH)_4^{2-}$ | -157.14 | -657.47 | [8] |
| $Cu_2(OH)_2^{2+}$ | -67.65 | -283.03 | [8] |
| $Cu_3(OH)_4^{2+}$ | -151.49 | -633.82 | [8] |
| $CuHCO_3^+$ | -127.09 | -531.73 | [9] |
| $CuCO_3^0$ | -119.84 | -501.43 | [9] |
| $Cu(CO_3)_2^{2-}$ | -251.19 | -1050.98 | [9] |
| $CuCO_3(OH)_2^{2-}$ | -206.00 | -861.90 | [10] |
| $Cu(OH)CO_3^-$ | -161.43 | -675.43 | [11] |
| $CuCl^+$ | -16.28 | -68.10 | [8] |
| $CuCl_2^0$ | -46.95 | -196.42 | [12] |

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[†] Lotus Development Corporation, Cambridge, MA.
[††] Microsoft Corporation, Redmond, WA.
[†††] Jandel Scientific, Inc., San Rafael, CA.
[††††] Golden Software, Inc., Golden, CO.

**TABLE 1 (Continued)**

| Species | $\Delta G_f^\circ$kcal/mol | $\Delta G_f^\circ$kJ/mol | Reference |
|---|---|---|---|
| $CuCl_3^-$ | -76.35 | -319.44 | [12] |
| $CuHPO_4^+$ | -250.14 | -1046.57 | [13] |
| $CuH_2PO_4^+$ | -256.61 | -1073.64 | [13] |
| $CuSO_4^0$ | -162.52 | -692.53 | [13] |
| $CuNH_3^{2+}$ | 3.80 | 15.92 | [13] |
| $Cu(NH_3)_2^{2+}$ | -7.21 | -30.16 | [13] |
| $Cu(NH_3)_3^{2+}$ | -17.36 | -72.65 | [13] |
| $Cu(NH_3)_4^{2+}$ | -25.72 | -107.59 | [13] |
| $Cu(NH_3)_5^{2+}$ | -32.06 | -134.14 | [13] |
| $CuNO_3^+$ | 14.97 | 62.63 | [8] |
| $Cu(NO_3)_2^0$ | 16.20 | 67.76 | [8] |
| $CuH_2P_2O_7^-$ | -468.47 | -1960.08 | [12] |
| $CuHP_2O_7^0$ | -463.16 | -1937.88 | [12] |
| $Cu_2P_2O_7$ | -427.31 | -1787.86 | [12] |
| $CuP_2O_7^{2-}$ | -451.96 | -1891.00 | [1] |
| $Cu(P_2O_7)_2^{6-}$ | -913.81 | -3823.40 | [1] |
| | Cu(II) Solids | | |
| CuO | -30.15 | -126.16 | [14] |
| CuO | -30.62 | -128.10 | [14] |
| CuO | -30.32 | -126.84 | [15] |
| $Cu(OH)_2$ | -85.60 | -358.16 | [14] |
| $Cu(OH)_2$ | -85.90 | -359.41 | [14] |
| $Cu(OH)_2$ | -85.22 | -356.56 | [15] |
| $CuCl_2$ | -56.29 | -232.52 | [13] |
| $Cu_2(OH)_3Cl$ | -160.09 | -669.83 | [13] |
| $Cu_4(OH)_6Cl_2$ (atacamite) | -320.51 | -1341.00 | [10] |
| $Cu_4(OH)_6Cl_2$ (paratacamite) | -320.27 | -1340.00 | [10] |
| $Cu_2(OH)_2CO_3$ (malachite) | -215.74 | -902.68 | [16] |
| $Cu_2(OH)_2CO_3$ (malachite) | -215.34 | -900.96 | [13] |
| $CuCO_3$ | -123.67 | -517.45 | [12] |
| $Cu_3(CO_3)_2(OH)_2$ (azurite) | -341.63 | -1429.36 | [12] |
| $CuSO_4$ (chalcocyanite) | -158.17 | -661.80 | [8] |
| $Cu_3(SO_4)(OH)_4$ (antlerite) | -345.75 | -1446.60 | [8] |
| $Cu_4(OH)_6(SO_4)\cdot H_2O$ (langite) | -488.53 | -2044.00 | [8] |
| $CuSO_4\cdot 5H_2O$ | -271.36 | -1135.37 | [12] |
| $CuO\cdot CuSO_4$ | 5.95 | 24.89 | [12] |
| $Cu_4(OH)_6SO_4$ (brochanite) | -434.51 | -1818.00 | [10] |
| $CuP_2O_7$ | -448.11 | -1874.91 | [12] |
| $Cu_2P_2O_7$ | -447.97 | -1874.30 | [8] |
| $Cu_3(PO_4)_2\cdot 2H_2O$ | -606.27 | -2536.62 | [12] |

## TABLE 1 (Continued)

| Species | $\Delta G_f^\circ$kcal/mol | $\Delta G_f^\circ$kJ/mol | Reference |
|---|---|---|---|
| $Cu_3(PO_4)_2$ | -490.30 | -2051.40 | [12] |
| $CuSiO_3 \cdot H_2O$ |  | -1207.50 | [10] |
| $CuSiO_3 . 2H_2O$ | -1443.90 | [10] |  |
|  | Associated Dissolved Species |  |  |
| $H^+$ | 0 |  |  |
| $O_2(g)$ | 0 |  |  |
| $O_2(aq)$ | 3.92 | 16.40 | [17] |
| $OH^-$ | -37.604 | -157.34 | [17] |
| $H_2CO_3$* | -148.95 | -623.21 | [17] |
| $HCO_3^{2-}$ | -140.28 | -586.93 | [17] |
| $CO_3^{2-}$ | -126.19 | -527.98 | [17] |
| $CO_2(g)$ | -94.257 | -394.37 | [17] |
| $H_3PO_3$ | -273.08 | -1,142.57 | [13] |
| $H_2PO_4^-$ | -269.80 | -1,128.84 | [13] |
| $HPO_4^{2-}$ | -260.313 | -1,089.15 | [13] |
| $H_2O$ | -56.690 | -237.19 | [17] |
| $PO_4^{3-}$ | -243.48 | -1,018.72 | [13] |
| $Cl^-$ | -31.380 | -131.29 | [17] |
| $F^-$ | -67.34 | -281.75 | [17] |
| $HSO_4^-$ | -180.66 | -755.88 | [17] |
| $SO_4^{2-}$ | -177.95 | -744.54 | [17] |
| $H_4SiO_4^0$ | -312.6 | -1,307.92 | [17] |
| $NO_3^-$ | -26.64 | -111.46 | [17] |
| $HOCl^0$ | -19.1 | -79.91 | [17] |
| $OCl^-$ | -8.8 | -36.82 | [17] |
| $Cl_2(aq)$ | 1.65 | 6.90 | [17] |
| $NH_3(aq)$ | -6.33 | -26.48 | [13] |

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11. Experimental log $\beta$ data determined at the ionic strength of sea water of: Symes, J.L. and D.R. Kester, Copper(II) Interaction with Carbonate Species Based on Malachite Solubility in Perchlorate Medium at the Ionic Strength of Seawater. Marine Chemistry, 1985. 16: p. 189-211, extrapolated to infinite dilution (I=0) using activity coefficient data of Byrne and Miller [9] for sea water, and estimating $\gamma$ for the complex as 0.65.

12. Derived from data given in: Lindsay, W.L., Chemical Equilibria in Soils. 1979, New York, New York: John Wiley & Sons. 449, through accepting log $\beta$ values, log K values, or computed $\Delta G_R°$ and rederiving $\Delta G_f°$ by substituting values for other reactant or product species from this table.

13. Computed from log $\beta$ values given in: Smith, R.M. and A.E. Martell, Critical Stability Constants. Vol. 4, Inorganic Ligands. 1976, New York: Plenum Press, using the Davies equation when necessary to extrapolate from values determined at $I \leq 0.5$ mol/L to I=0.

14. Computed from log K or log $\beta$ values given in: Schindler, P.W., Heterogeneous Equilibria Involving Oxides, Hydroxides, Carbonates and Hydroxide Carbonates, in Equilibrium Concepts in Natural Water Systems. 1967, American Chemical Society: Washington, DC., after correcting to I=0 by the Davies equation.

15. Computed from log K data given by: de Zoubov, N., C. Vanleugenhaghe, and M. Pourbaix, Copper, in Atlas of Electrochemical Equilibria in Aqueous Solutions. 1974, National Association of Corrosion Engineers: Houston, TX. p. 384-392.

16. Computed from log K data in: Symes, J.L. and D.R. Kester, Thermodynamic Stability Studies of the Basic Copper Carbonate Mineral, Malachite. Geochim. Cosmochim. Acta, 1984. 48: p. 2219-2229.

17. From the table of $\Delta G_f°$ values in: Schock, M.R. and I. Wagner, The Corrosion and Solubility of Lead in Drinking Water, in Internal Corrosion of Water Distribution Systems, 4, Editor. 1985, AWWA Research Foundation/DVGW Forschungsstelle: Denver, CO.

Table 2 gives a listing of the fundamental equilibrium reactions incorporated into the Cu(I) solubility spreadsheet and CU2SOL Fortran programs used to construct speciation and solubility diagrams for this paper. These constants were computed from the $\Delta G_f°$ data from Table 1.

## TABLE 2. EQUILIBRIUM REACTIONS IN COPPER SOLUBILITY PROGRAMS, AND CORRESPONDING LOG K AND LOG $\beta$ VALUES

| Reaction | log K or $\beta$ at 25° |
|---|---|
| *Copper(I) Species* | |
| $Cu^\circ \leftrightarrow Cu^+ + e^-$ | -8.760 |
| $Cu^+ + Cl^- \leftrightarrow CuCl^-$ | 2.70 |
| $Cu^+ + 2Cl^- \leftrightarrow CuCl^\circ$ | 5.48 |
| $Cu^+ + 3Cl^- \leftrightarrow CuCl_3^{2-}$ | 4.81 |
| $2Cu^+ + 4Cl^- \leftrightarrow Cu_2Cl_4^{2-}$ | 10.32 |
| $Cu^+ + NH_3^\circ \leftrightarrow CuNH_3^+$ | 5.9 |
| $Cu^+ + 2NH_3^\circ \leftrightarrow Cu(NH_3)_2^+$ | 10.8 |
| $Cu_2O(S) + 2H^+ \leftrightarrow 2Cu^+ + H_2O$ | -1.62 |
| $CuOH(S) + H^+ \leftrightarrow Cu^+ + H_2O$ | 0.91 |
| *Copper(II) Species* | |
| $Cu^+ \leftrightarrow Cu^{2+} + e^-$ | -2.715 |
| $Cu^{2+} + H_2O \leftrightarrow CuOH^+ + H^+$ | -7.96 |
| $Cu^{2+} + 2H_2O \leftrightarrow Cu(OH)_2^\circ + 2H^+$ | -16.24 |
| $Cu^{2+} + 3H_2O \leftrightarrow Cu(OH)_3^- + 3H^+$ | -26.90 |
| $Cu^{2+} + 4H_2O \leftrightarrow Cu(OH)_4^{2-} + 4H^+$ | -39.56 |
| $2Cu^{2+} + 2H_2O \leftrightarrow Cu_2(OH)_2^{2+} + 2H^+$ | -10.58 |
| $3Cu^{2+} + 4H_2O \leftrightarrow Cu_3(OH)_4^{2+} + 4H^+$ | -20.76 |
| $Cu^{2+} + H^+ + CO_3^{2-} \leftrightarrow CuHCO_3^+$ | 12.13 |
| $Cu^{2+} + CO_3^{2-} \leftrightarrow CuCO_3^\circ$ | 6.82 |
| $Cu^{2+} + 2CO_3^{2-} \leftrightarrow Cu(CO_3)_2^{2-}$ | 10.60 |
| $Cu^{2+} + CO_3^{2-} + H_2O \leftrightarrow Cu(OH)CO_3^- + H^+$ | -4.25 |
| $Cu^{2+} + CO_3^{2-} + 2H_2O \leftrightarrow Cu(OH)_2CO_3^{2-} + 2H^+$ | -13.14 |
| $Cu^{2+} + 2H^+ + PO_4^{3-} \leftrightarrow CuH_2PO_4^+$ | 21.09 |
| $Cu^{2+} + H^+ + PO_4^{3-} \leftrightarrow CuHPO_4^\circ$ | 16.35 |
| $Cu^{2+} + SO_4^{2-} \leftrightarrow CuSO_4^\circ$ | 2.36 |
| $Cu^{2+} + NH_3 \leftrightarrow Cu(NH_3)^{2+}$ | 4.04 |
| $Cu^{2+} + 2NH_3 \leftrightarrow Cu(NH_3)_2^{2+}$ | 7.47 |
| $Cu^{2+} + 3NH_3 \leftrightarrow Cu(NH_3)_3^{2+}$ | 10.27 |
| $Cu^{2+} + 4NH_3 \leftrightarrow Cu(NH_3)_4^{2+}$ | 11.75 |
| $Cu^{2+} + 5NH_3 \leftrightarrow Cu(NH_3)_5^{2+}$ | 11.76 |
| $Cu^{2+} + Cl^- \leftrightarrow CuCl^+$ | 0.40 |
| $Cu^{2+} + 2Cl^- \leftrightarrow CuCl^\circ$ | -0.12 |
| $CuO(s) + 2H^+ \leftrightarrow Cu^{2+} + H_2O$ | 7.98 |
| $Cu(OH)_2(s) + 2H^+ \leftrightarrow Cu^{2+} + 2H_2O$ | 8.89 |
| $CuCO_3(s) \leftrightarrow Cu^{2+} + CO_3^{2-}$ | -9.63 |
| $Cu_2(OH)_2CO_3(s) + 2H+ \leftrightarrow 2Cu^{2+} + 2H_2O + CO_3^{2-}$ | -5.48 |
| $Cu_3(PO_4)_2 \bullet 2H_2O(s) \leftrightarrow 3Cu^{3+} + 2PO_4^{3-} + 2H_2O$ | -38.76 |
| $Cu_3(PO_4)_2(s) \leftrightarrow 3Cu^{3+} + 2PO_4^{3-}$ | -36.86 |

**TABLE 2 (Continued)**

| Reaction | log K or $\beta$ at 25° |
|---|---|
| $Cu_3SO_4(OH)_4(s) + 4H^+ \leftrightarrow 3Cu^{2+} + SO_4^{2-} + 4H_2O$ | 8.81 |
| $Cu_4SO_4(OH)_6(s) + 6H^+ \leftrightarrow 4Cu^{2+} + SO_4^{2-} + 6H_2O$ | 15.38 |
| $Cu_2(OH)_3Cl(s) + 3H^+ \leftrightarrow 2Cu^{2+} + Cl^- + 3H_2O$ | 14.68 |
| $Cu_4SO_4(OH)_6 \bullet H_2O + 6H^+ \leftrightarrow 4Cu^{2+} + SO_4^{2-} + 7H_2O$ | 17.34 |
| *Related Reactions* | |
| $H_2CO_3^* \leftrightarrow H^+ + HCO_3^-$ | 6.352 |
| $HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$ | 10.329 |
| $H_2O \leftrightarrow H_+ + OH_-$ | 13.995 |
| $H_3PO_4 \leftrightarrow H^+ + H_2PO_4^-$ | 2.155 |
| $H_2PO_4^- \leftrightarrow H_+ HPO_4^{2-}$ | 7.207 |
| $HPO_4^- \leftrightarrow H^+ + PO_4^{3-}$ | 12.346 |
| $NH_4^+ \leftrightarrow H^+ + NH_3^\circ$ | -9.252 |
| $HSO_4^- \leftrightarrow H^+ + SO_4^{2-}$ | 1.99 |

## Oxidation Reactions of Copper

Copper metal from pipe and alloys is readily oxidized in contact with most drinking waters. Copper may exist in water in either the monovalent copper(I) (cuprous) or divalent copper(II) (cupric) valence states. The copper(III) and copper(IV) valence states are known to exist, however, they occur at high temperature and usually in the presence of high oxygen concentrations[24] and are not expected in drinking water. No reports of their production under natural water and water supply conditions have been located. In potable waters, copper metal may undergo the following two basic electrochemical transformations:

$$Cu(s) \leftrightarrow Cu^+ + e^- \tag{1}$$

$$Cu^+ \leftrightarrow Cu^{2+} + e^- \tag{2}$$

Because of the positive cell potentials for copper metal oxidation, copper pipe in water containing dissolved oxygen will continue to corrode until all of the oxygen is depleted, or until precipitated oxide films arrest the rate of corrosion.[25] There is some evidence that the overall transformation from $Cu^+$ to $Cu^{2+}$ is essentially the rate-limiting factor, with $Cu^+$ existing essentially in reversible equilibrium with the Cu metal at the pipe surface.[26]

In drinking waters, the oxidizing agents (electron acceptors) that will cause the corrosion of metallic copper are predominantly dissolved oxygen and aqueous chlorine species.[12,27,28] Following are several possible net reactions for the corrosion of copper in drinking waters. These reactions may be composed of several intermediate steps, any of which can be rate-controlling.

$$HOCl^\circ + H^+ + Cu(s) \leftrightarrow Cu^{2+} + Cl^- + H_2O \tag{3}$$

$$OCl^- + 2H^+ + Cu(s) \leftrightarrow Cu^{2+} + Cl^- + H_2O \tag{4}$$

$$Cu(s) + \tfrac{1}{2} O_2 + 2H^+ \leftrightarrow Cu^{2+} + H_2O \tag{5}$$

The overall corrosion potential driving force for any of equations (3) through (5) may be computed through the Nernst equation.[14,15,29-31] For pure solids and in dilute aqueous solution, the activities of the solid copper metal and that of water may be assumed to be equal to unity. Thus, the expression (4), for example, becomes

$$E = E^\circ - 2.303 \frac{RT}{2F} \log \frac{\gamma_{Cl^-}[Cl^-]\gamma_{Cu^{2+}}[Cu^{2+}]}{\gamma_{OCl^-}[OCl^-]\gamma^2_{H^+}[H^+]^2} \tag{6}$$

in Nernst form. After half-cell reactions are combined, their potentials added, and constants evaluated, the resulting expression becomes:

$$E = 1.38 - 0.0296 \log \frac{\gamma_{Cl^-}[Cl^-]\gamma_{Cu^{2+}}[Cu^{2+}]}{\gamma_{OCl^-}[OCl^-]\gamma^2_{H^+}[H^+]^2} \tag{7}$$

The symbols in equations (6) and (7) have their conventional meanings: E, the cell potential in volts; E° the standard reduction potential for the overall reaction in volts; R the gas constant; T, the temperature in Kelvins; and F, the Faraday constant. The number 2 in the denominator of (6) reflects the 2 electron transfer for the oxidation reaction of copper metal to cupric ion in equation (4). Similar Nernst equations can be derived and computed for alternate oxidants. Note also that only the free ion activities are important to the equation, so complexation by carbonate, sulfate, etc. must be computed to enable the isolation of the free hydrogen, chloride, and cupric ions that dictate the voltage for this redox couple undergoing corrosion.

Many papers and texts have documented the impact of dissolved oxygen on copper oxidation and dissolution rates. Several studies have also proven aqueous chlorine species have a significant impact on the copper oxidation and corrosion rates.[27,28,32-34] Free chlorine species (ie. $HOCl^\circ$, $OCl^-$, $Cl_2$) have not been conclusively shown to affect the equilibrium solubility of copper, other than by influencing the valence state of the copper by its presence or absence.

Oxidants may have several other potential impacts on the observed copper levels in the water and the nature of the passivating solids on the pipe. The effect of chlorine on the oxidation rate of the copper metal might be alteration of the crystalline characteristics and porosity of the oxide corrosion product film produced at the pipe surface, such as by reducing the formation of a protective $Cu_2O(s)$ underlayer by producing a high $E_H$ level, or by indirectly influencing scale structure and conductivity through chloride formation as the chlorine is reduced.[17] However, many of the apparent effects of chlorine on copper solubility may merely result from accelerated corrosion kinetics (rates), rather than changes in equilibrium conditions. That is, the rate of copper oxidation and transport into solution may be accelerated by the oxidants, misinterpreted as representing a greater equilibrium solubility. If the stagnation curve was controlled purely by ionic diffusion of cupric or cuprous aqueous species, it would follow the model delineated by Kuch and Wagner,[35] which would be independent of oxidant concentration above a threshold redox potential that causes oxidation of the base copper piping.

The relative stabilities of Cu(I) and Cu(II) species in aqueous solution depend very strongly on the nature of anions or other ligands present in the water. In pure water, cuprous ion is unstable in the presence of an oxidizing agent such as oxygen, and cupric ion is formed by the disproportionation reaction.[12,24]

$$2Cu^{+} \leftrightarrow Cu(s) + Cu^{2+} \tag{8}$$

Therefore, when cuprous species are present in water, they probably result from stabilization through the formation of various aqueous complexes.

Specific research into the redox potential (ie., $E_H$ or pE) of drinking waters in general has not been reported. Some indirect information to estimate the level for some systems may be gathered, however. For disinfected systems, the redox potential will be dominated by the aqueous chlorine (or other oxidant) species involved. Hypochlorous acid and hypochlorite ion have $E_H$/pH stability fields that are above the equilibrium line for water with oxygen in the atmosphere.[14,30,31] This fact explains the tendency for even pure water to lose its chlorine residual over time in plumbing.

Several studies have attempted to measure the redox potential ($E_H$) of waters dosed with varying levels of chlorine, chloramines, ozone, or other disinfectants.[36-39] The resulting $E_H$ values generally fell into the range of 0.6 to 1.2 V versus SHE (standard hydrogen electrode). The potentials were a function of the individual or mix of disinfectant species, their concentrations, and time. As expected, this $E_H$ range is higher than that attainable with typical dissolved oxygen levels in drinking waters. Most surface water supplies will have undergone disinfection, so their redox potentials will range from a low controlled by the dissolved oxygen in the system, to a high controlled by the disinfection species.

For domestic or municipal water systems using wells, however, the redox potential could encompass a wider range. Other oxidation processes, such as greensand filtration or aeration (for iron and manganese removal) may cause the resulting redox potential to remain higher and the residual oxidant concentrations may be stable longer. Granular activated carbon (GAC) removes many substances that consume oxidants. Other substances that can influence corrosion and lower redox potentials include organic matter, nitrogen species, sulfur species, iron species, or even microorganisms.[40,41]

Considerable attention has been paid to factors governing the redox potential of natural systems, and problems inherent in its measurement.[15,40,41] A precise range of redox potential values for the wide variety of ground water conditions across the United States cannot be given, but some limits can be estimated. In the pH range of 5 to 8, then, $E_H$ values could likely be in the neighborhood of -0.2 V as a general lower limit.

Copper plumbing, therefore, can be exposed to a wide environment of $E_H$-pH conditions. This environment evolves, as oxidation and reduction reactions occur through corrosion and deposition processes for different lengths of stagnation times, and in different diameters of pipes. Therefore, all three normal copper valence states (metal, +1, +2) could reasonably occur under drinking water conditions either geographically or with time.

### The Conceptual Role of Aqueous Complexation

The inclusion of appropriate aqueous complexes in the chemical model is essential to enable accurate prediction of metal solubilities. For copper, a more than 100-fold negative error in predicted equilibrium copper solubility is introduced by the neglect of the $Cu(OH)_2^\circ$ complex, even if other hydrolysis species are included.[42] An even greater error is introduced in both the magnitude and trend of solubility when only the free cupric ion ($Cu^{2+}$) is assumed to be present. In virtually all drinking waters, at least some DIC (dissolved inorganic carbonate) is present. Because Cu(II) (cupric form) forms several very strong and some weaker aqueous complexes with carbonate species ($HCO_3^-$, $CO_3^{2-}$), carbonate complexation tends to become even more important that the hydrolysis reactions as the pH increases, especially above a pH of about 7.

### Copper (I) Chemistry

In the absence of oxygen and added oxidants, water does not corrode copper. That is because the immune region for copper corrosion extends well above the minimum $E_H$ for water stability.[12,29,43] With the addition of electron acceptors to the solution (eg. $HOCl^\circ$, $O_2$), either or both of the oxide solids $Cu_2O$ (cuprite) or Cu(OH) may form. Given the variety of different crystalline oxides of these solids that may form, differences in reported solubilities are significant enough to cause prediction uncertainties for cuprous solubility of roughly 10 to 100. Additionally, the conditions under which protective oxide layers form are poorly known.[29] Identifying the solid is further complicated by oxidation and dehydration that might accompany some of the normal sample preparation steps for analysis by X-Ray diffraction or other instrumental techniques. The transformation from cuprous hydroxide to cuprous oxide at the pipe surface is also likely to be affected by hydrodynamic factors, and both the nature and concentrations of ions in solution. Some research has indicated that $Cu_2O(s)$ may be formed below the surface of existing corrosion byproduct deposits under oxidizing conditions, through rapid $Cu(OH)_2(s)$ dissolution followed by disproportionation and redeposition of $Cu_2O(s)$[44]. Hydrodynamic conditions are very important in this situation, which might also affect the crystallinity of the $Cu(OH)_2(s)$ and its conversion to more stable CuO(s).[45] This is most favored in fractures and crevices of the surface film, and helps explain the formation of layered copper corrosion deposits that have cupric solids on the surface with $Cu_2O(s)$ underneath. Le Gal La Salle, *et. al.* have also done electrochemical studies that indicate a cyclic transformation of rapidly formed $Cu^+$ and $Cu^{2+}$ cations, compact $Cu_2O(s)$ layer, and then the reoxidation and formation of a porous external layer of CuO(s) or $Cu(OH)_2(s)$.[46]

Cuprous ion forms very weak hydrolysis species (ie. $CuOH^\circ$), if any. No species of this type are generally reported in relevant reviews of copper chemistry,[29,47-49] so they are not included in this solubility model. The formation of bicarbonate and carbonate complexes ($CuHCO_3^\circ$ and $CuCO_3^-$, respectively) have been hypothesized to explain some trends in rates of oxidation by dissolved oxygen, but no experimentally determined values or ones estimated from thermodynamic principles are available.[50]

Despite these uncertainties, cuprous aqueous chemistry appears to be dominated by the formation of several stabilizing complexes. Notably, two are particularly significant in drinking water: $NH_3$ and $Cl^-$. Cuprous ammine complexes can be formed either directly, or by reduction of cupric ammine complexes by a route such as this:[24]

$$\left[Cu(NH_3)_4{}^{2+}\right] + Cu(s) \leftrightarrow 2\left[Cu(NH_3)_2{}^{+}\right] \tag{9}$$

Also, complexes of Cu(I) are generally formed by direct interaction of ligands with copper(I) halides and reduction of Cu(II) compound, or reduction of $Cu^{2+}$ in presence of the ligand.[24] Rickard has concluded from various complexation experiments and observations of geochemical mineral assemblages that even in the presence of strong oxidants, ammonia can increase the solubility of oxide, hydroxide, oxysulfate, oxycarbonate and oxychloride solids of copper.[51,52] This results from the stabilization of the cuprous form of copper in solution through the formation of the diamminecuprous ion, $[Cu(NH_3)_2]^+$. Similarly, in the presence of fairly high concentrations of ammonium salts, the domain of stability of dissolved copper(I) species, and hence the domain of corrosion, expands considerably.[29,52] Severe attack of copper pipe attributed to the presence of high concentrations of ammonia in the soldering flux has also been noted.[53]

Cuprous chloride complexes are not as strong as the ammine complexes, but they may be significant because chloride concentrations are many times those of ammonia in most drinking waters. They have been shown to play an important role in retarding the rate of cuprous ion oxidation in natural waters, particularly at neutral to alkaline pH's.[50,54-57] Presumably, this effect would also apply to the drinking water environment under similar chemical conditions. The equilibrium solubility of cuprous copper, $S_{T,Cu(I)}$, may be described as the sum of the concentrations of all dissolved cuprous species:

$$\begin{aligned} S_{T,Cu(I)} = & \left[Cu^+\right] + \left[CuCl^\circ\right] + \left[CuCl_2^-\right] + \left[CuCl_3^{2-}\right] + \left[Cu_2Cl_4^{2-}\right] \\ & + \left[Cu(NH_3)^+\right] + \left[Cu(NH_3)_2^+\right] \end{aligned} \tag{10}$$

In which [ ] (brackets) indicate concentration in mol/L. The total solubility may then be computed by standard techniques[14,15,21,30,31]. The concentrations of all aqueous species may be expressed in terms of the concentrations of the metal and ligand and the formation constant for the complex, valid for a particular temperature and ionic strength. Thus, equation (10) can be rewritten as:

$$S_{T,Cu(I)} = \left[Cu^+\right] + \beta'_{Cl,11}\left[Cu^+\right]\left[Cl^-\right] + \beta'_{Cl,12}\left[Cu^+\right]\left[Cl^-\right]^2 + \beta'_{Cl,13}\left[Cu^+\right]\left[Cl^-\right]^3 + \beta'_{Cl,24}\left[Cu^+\right]^2\left[Cl^-\right]^4 + \beta_{NH_3,11}\left[Cu^+\right]\left[NH_3\right] + \beta'_{NH_3,12}\left[Cu^+\right]\left[NH_3\right]^2 \qquad \textbf{(11)}$$

in which $\beta'$ represents the conditional overall formation constant corrected for ionic strength and temperature.

For the purpose of this calculation, the formation of the solid CuOH(s) is assumed to control the activity of free cuprous ion at equilibrium as follows:

$$\left[Cu^+\right] = \frac{K_{s,CuOH}\left[H^+\right]\gamma_{H^+}}{\gamma_{Cu^+}} \qquad \textbf{(12)}$$

Given that the activity of water and the solid are unity, the activity coefficient terms can be incorporated into a conditional solubility constant, $K'_{s,CuOH}$, analogous to the conditional stability constants used in expression (11). The resulting expression (13) may be substituted for each of the $[Cu^+]$ terms in equation (11), to yield the final equation programmed for calculation.

$$\left[Cu^+\right] = K'_{s,CuOH}\left[H^+\right] \qquad \textbf{(13)}$$

Figures 1 and 2 show the effect of chloride and ammonia complexation on copper (I) solubility at 25°C, assuming CuOH to be the solubility-controlling solid. If the solid $Cu_2O$ phase (cuprite) controlled the solubility, it would lower the predicted Cu(I) solubility by a factor of about 60 to 100. However, it would not affect the trends of the solubility curves. Clearly, when oxidizing power in the solution is absent, levels of chloride and ammonia found in many water supplies could significantly increase soluble copper concentrations.

## Copper(II) Hydrolysis Reactions

Major inconsistencies exist among most published hydrolysis and complexation formation constants for the cuprous ion, particularly for the complex $Cu(OH)_2^\circ$. Reported values for log $\beta$ have been found ranging from -13.7 to "less than-17.3" for the reaction:

$$Cu^{2+} + 2H_2O \leftrightarrow Cu(OH)_2^\circ + 2H^+ \qquad \textbf{(14)}$$

To compound the problem, data either conflict or there are very few reports of any determinations of stability constants for the possible complexes $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$. These complexes could be of significance in waters of pH of approximately 9 and above. Thus, these values must be treated with some skepticism. The confusion is exemplified by the critical evaluation of existing data done by Baes and Mesmer.[47] They could not select what they considered to be definitive values for the formation constants of $CuOH^+$, $Cu(OH)_2^\circ$, or $Cu(OH)_3^-$, all of which could be either

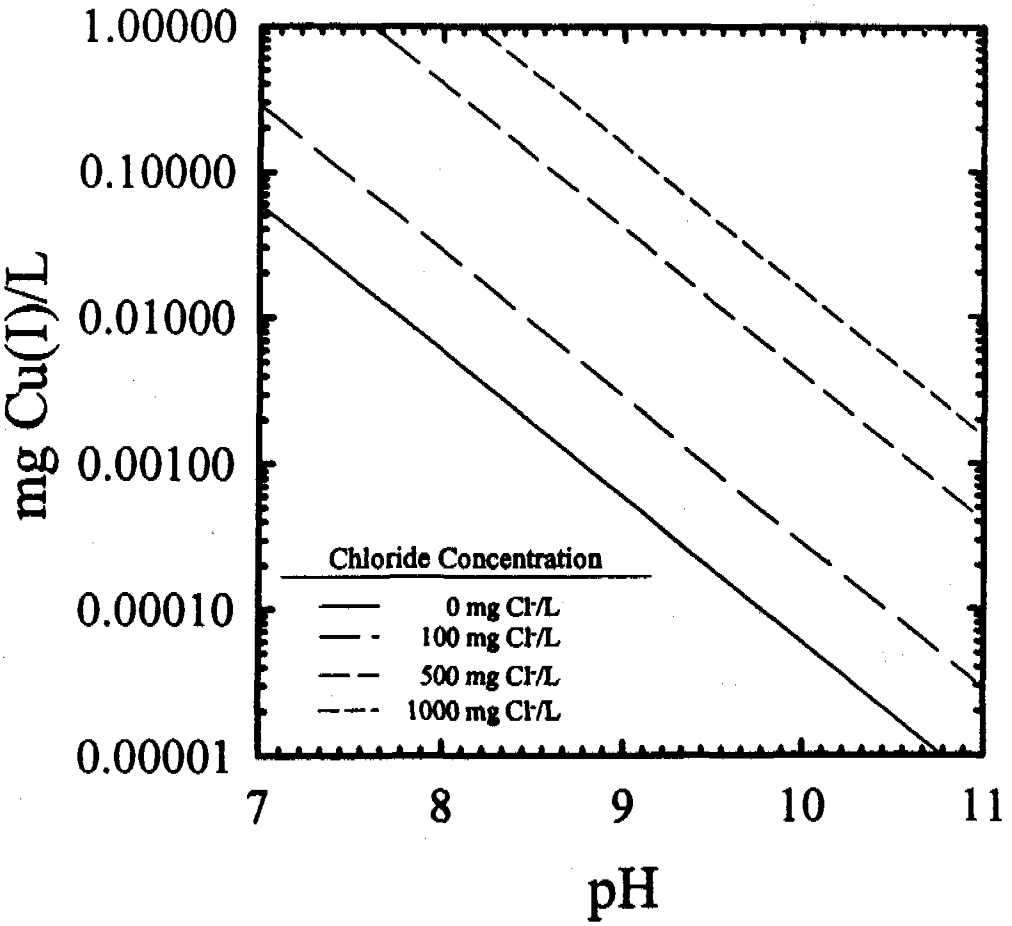

Figure 1. Effect of chloride complexation on CuOH(s) solubility, I=0.02, 25°C.

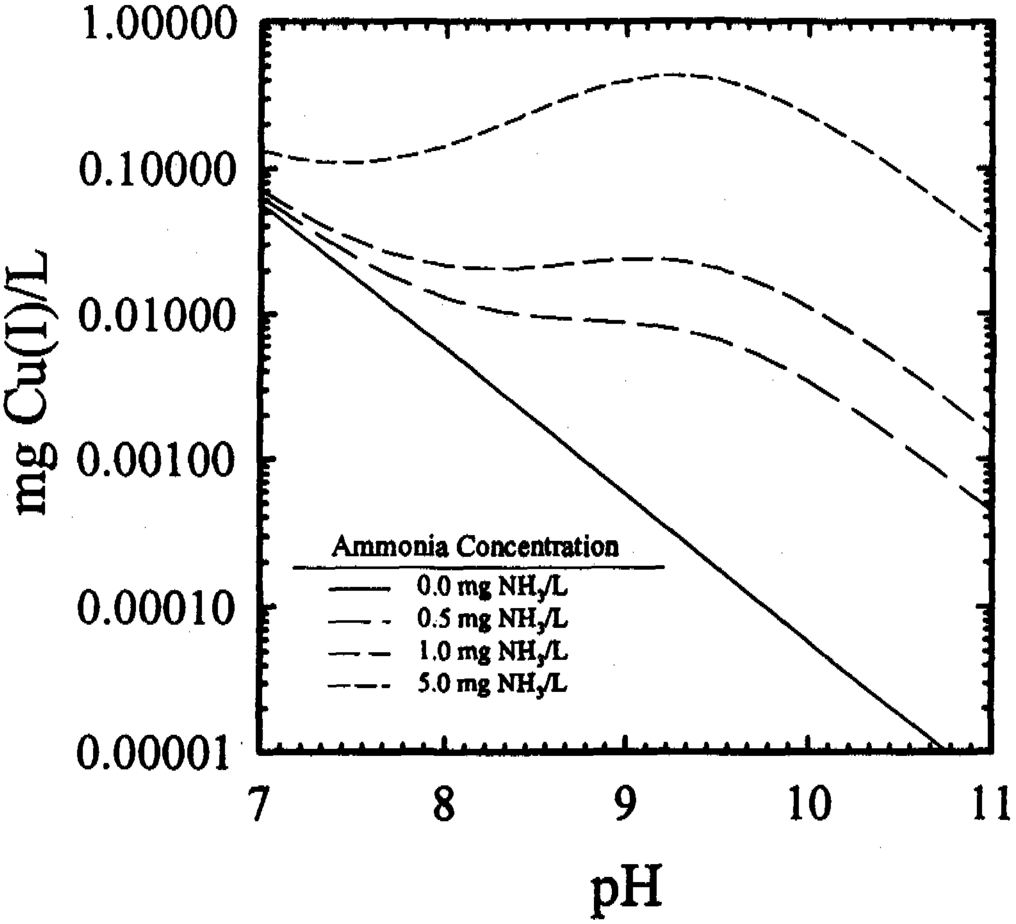

Figure 2. Effect of ammonia complexation on CuOH(s) solubility, I=0.01, 25°C.

directly or indirectly significant in drinking waters. They only chose to report limits on the likely magnitudes of the respective log $\beta$ constants (eg. "<-8,", "<-17.3", "<-27.8"), which unfortunately encompasses almost all of the values reported for these species. Very little additional research has been conducted in recent years. Table 3 indicates some of the reported log $\beta$ values in the literature for the $Cu(OH)_2^\circ$ complex, and illustrates the uncertainty of any selected value.

**TABLE 3. A SELECTION OF REPORTED LOG $\beta_{12}$ VALUES FOR THE REACTION: $Cu^{2+} + 2H_2O \leftrightarrow Cu(OH)_2^\circ + 2H^+$**

| Log $\beta$12 | Reference |
|---|---|
| <-17.3 | [1] |
| -16.22 | [2] |
| -16.24 | [3] |
| -14.70 | [4] |
| -13.7 | [5] |

References

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The background solubility of cupric copper under oxidizing conditions resulting from the unavoidable hydrolysis reactions is completely defined by the simple total solubility expression ($S_{T,OH}$), which includes the free cupric ion concentration [$Cu^{2+}$].

$$\begin{aligned} S_{T,OH} = & \left[Cu^{2+}\right] + \left[CuOH^+\right] + \left[Cu(OH)_2{}^\circ\right] + \left[Cu(OH)_3{}^-\right] + \\ & \left[Cu(OH)_4^{2-}\right] + 2\left[Cu_2(OH)_2^{2+}\right] + 3\left[Cu_3(OH)_4^{2+}\right] \end{aligned} \tag{15}$$

After substituting rearranged complexation expressions from Table 2 in terms of concentrations with equilibrium constants corrected for ionic strength and temperature, as was done for Equation 11, the complete expression is:

$$S_{T,OH} = \left[Cu^{2+}\right] + \frac{\beta'_{1,1}\left[Cu^{2+}\right]}{\left[H^{+}\right]} + \frac{\beta'_{1,2}\left[Cu^{2+}\right]}{\left[H^{+}\right]^{2}} + \frac{\beta'_{1,3}\left[Cu^{2+}\right]}{\left[H^{+}\right]^{3}} + \frac{\beta'_{1,4}\left[Cu^{2+}\right]}{\left[H^{+}\right]^{4}} + 2\frac{\beta'_{2,2}\left[Cu^{2+}\right]^{2}}{\left[H^{+}\right]^{2}} + 3\frac{\beta'_{3,4}\left[Cu^{2+}\right]^{3}}{\left[H^{+}\right]^{4}} \tag{16}$$

assuming the activity of $H_2O$ is 1.

## Copper(II) Complexation by Carbonate

Considerable research has been devoted to the study of the aqueous speciation of copper in natural waters and seawater, in which the role of carbonate species was extremely important.[19,20,51,58-61] The concept of the significance of carbonate complexation was then applied to potable waters by Schock, with indications that high DIC levels would aggravate cuprosolvency.[22,62] Most of these solubility models presumed that $Cu_2(OH)_2CO_3$ (malachite) was the solid phase governing equilibrium solubility. Interestingly, though Pourbaix and colleagues did not originally consider carbonate complexes in their pioneering work on $E_H$-pH relationships involved in copper corrosion,[29,63] they were ultimately added to the calculations.[43] Unfortunately, few engineers and corrosion scientists in the United States noticed the revision of the $E_H$-pH diagrams, so much misinformation about improved passivation through substantial DIC addition has continued to appear in articles, textbooks, and manuals.

The selection of the aqueous carbonate species to be incorporated into this solubility model follows the selections of Byrne and Miller[60] and Stiff.[64] There is a considerable spread in the reported constants for $Cu(CO_3)_2^{2-}$ and $CuHCO_3^+$, as is shown in Table 4, which lists many of the reported log $\beta$ values for cupric bicarbonate, carbonate, and hydroxycarbonate complexes. Exploratory calculations showed that the $CuCO_3(OH)_2^{2-}$ complex species reported in an uncritical compilation of $\Delta G_f^\circ$ values, may have an important impact on copper solubility at pH levels found in many lime-softened or other high-pH water supplies. Therefore, it was included in this revised model, pending speciation information to the contrary. The contribution to copper(II) solubility from carbonate species, $S_{T,CO_3}$ is described by the expression:

$$S_{T,CO_3} = \left[CuHCO_3^{+}\right] + \left[CuCO_3^{\circ}\right] + \left[Cu(CO_3)_2^{2-}\right] + \left[CuCO_3OH^{-}\right] + \left[Cu(CO_3)_2(OH)_2^{2-}\right] \tag{17}$$

**TABLE 4. A SELECTION OF REPORTED LOG EQUILIBRIUM CONSTANTS (SS) FOR COPPER (II) CARBONATE COMPLEXES. ALL VALUES HAVE BEEN REPORTED FOR 25°C AND I=0, OR WERE EXTRAPOLATED TO I=0 BY THE DAVIES EQUATION FOR I≤0.5**

| Log $\beta^\dagger$ | | | | |
|---|---|---|---|---|
| $CuHCO_3^+$ | $CuCO_3^\circ$ | $Cu(CO_3)_2^{2-}$ | $CuCO_3OH^-$ | Reference |
| 12.41 | — | — | — | [1] |
| 12.13 | 6.82 | 10.6 | -4.5 | [2] |
| — | 6.86 | 10.71 | — | [3] |
| 12.53 | — | — | — | [4] |
| — | 6.71 | 9.01 | — | [5] |
| — | 6.75 | — | — | [5] |
| — | 6.73 | 9.83 | — | [6] |
| — | 6.74 | 10.23 | — | [7] |
| — | 6.80 | — | — | [8] |
| — | 6.34 | — | — | [9] |
| — | 6.77 | 10.11 | — | [10] |
| 12.43 | — | — | — | [11] |
| 11.63 | — | — | — | [12] |
| — | — | — | -4.25 | [13] |
| — | 6.75 | 10.69 | — | [14] |
| 13.83 | 6.89 | — | — | [15] |
| 13.03 | — | — | — | [16] |

†For the reactions

$$Cu^{2+} + H^+ + CO_3^{2-} \leftrightarrow CuHCO_3^+ + H_2O$$

$$Cu^{2+} + CO_3^{2-} \leftrightarrow CuCO_3^\circ$$

$$Cu^{2+} + 2CO_3^{2-} \leftrightarrow Cu(CO_3)_2^{2-}$$

$$Cu^{2+} + H_2O + CO_3^{2-} \leftrightarrow CuCO_3OH^- + H^+$$

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In an analogous manner to the cupric hydrolysis reactions above, the concentrations of each of these complexes can be expressed in terms of only [$Cu^{2+}$], [$H^+$], and [$CO_3{}^{2-}$], as follows:

$$Cu^{2+} + CO_3{}^{2-} + H^+ \leftrightarrow CuHCO_3{}^+ \tag{18}$$

$$Cu^{2+} + CO_3{}^{2-} \leftrightarrow CuCO_3{}^{\circ} \tag{19}$$

$$Cu^{2+} + 2CO_3{}^{2-} \leftrightarrow Cu(CO_3)_2^{2-} \tag{20}$$

$$Cu^{2+} + CO_3{}^{2-} + H_2O \leftrightarrow CuCO_3OH^- + H^+ \tag{21}$$

$$Cu^{2+} + Co_3{}^{2-} + 2H_2O \leftrightarrow CuCO_3(OH)_2^{2-} + 2H^+ \tag{22}$$

Making the rearrangement and corresponding substitutions of equations (18) through (22) into equation (16) based on reactions written by this convention yields equation (23):

$$\begin{aligned} S_{T,CO_3} = {} & \beta'_{1,1,1}[Cu^{2+}][H^+][CO_3{}^{2-}] + \beta'_{1,0,1}[Cu^{2+}][CO_3{}^{2-}] + \beta'_{1,0,2}[Cu^{2+}][CO_3{}^{2-}]^2 + \\ & \frac{\beta'_{1,-1,1}[Cu^{2+}][CO_3{}^{2-}]}{[H^+]} + \frac{\beta'_{1,-2,1}[Cu^{2+}][CO_3{}^{2-}]}{[H^+]^2} \end{aligned} \tag{23}$$

in which the formation constants ($\beta'$) are corrected for ionic strength and temperature, and the negative numbers in the subscript for hydrogen ion indicate hydroxide ions in the complex. The total solubility of copper(II) in pure water containing carbonate as the only complexing family of ligands is then given by $S_{T,Cu(II)}$:

$$S_{T,Cu(II)} = S_{T,OH} + S_{T,CO_3} \qquad \textbf{(24)}$$

### *Passivating Cupric Oxide and Hydroxide Solids*

The quantitative prediction of copper levels in drinking water, made much more important by recent U. S. Environmental Protection Agency regulations,[1-3] relies heavily on the solubility and physical properties of cupric oxide, hydroxide and basic carbonate solids that comprise most scales in water supplies. Because of considerable uncertainty in the values for the solubility constants of all of these minerals, the tendency for prolonged existence of thermodynamically metastable phases such as $Cu(OH)_2(s)$, and the possibly slow formation rate of $Cu_2(OH)_2CO_3(s)$ (malachite), quantitation becomes highly problematic.

The differences among several solubility constants for CuO(s) and $Cu(OH)_2(s)$ have been discussed by de Zoubov, *et. al.*, who selected two constants that they felt best agreed with actual copper solubility data.[29] In their critical evaluation of hydrolysis behavior of almost all important environmental metals, Baes and Mesmer[47] selected somewhat different values, which were an outgrowth of the research of Schindler, *et. al.* on particle size effects and the solubility of oxides and hydroxides.[31,65,66] This intriguing work by Schindler *et. al.* on the relationship of the solubility and solubility constant for CuO(s) and $Cu(OH)_2(s)$ to a parameter called "molar surface" (units of $m^2$) may provide another avenue of important insight into the discrepancies among the reported thermodynamic constants.[65,66] Essentially, the molar surface is related through various parameters to the surface area of particles of a solid, such that as the size of the particles decreases, the molar surface increases. Increases in the molar surface are physically related to the thermodynamic property Gibbs free energy, which governs the intrinsic solubility of the solid and its stability relative to other crystalline forms of the same solid.[31,65,66] Schindler, et. al. found the log equilibrium constant for the solubility reaction

$$Cu(OH)_2(s) + 2H^+ \leftrightarrow Cu^{2+} + 2H_2O \qquad \textbf{(25)}$$

to vary from 8.92 to 9.13 at I=0.2, as the molar surface increased from 0 to 4570 $m^2$. If these constants are corrected to zero ionic strength, using the Davies equation,[15,41,67] the range is 8.67 to 8.89, respectively. Similarly, they found the log equilibrium constant for the tenorite solubility reaction

$$CuO(s) + 2H^+ \leftrightarrow Cu^{2+} + H_2O \qquad \textbf{(26)}$$

to vary from 7.89 to 8.27 at I=0.2, as the molar surface rose from 0 to 4340 $m^2$. Correcting for ionic strength using the Davies equation,[15,41,67] the range is 7.64 to 7.98. Particle size effects may therefore have significantly contributed to scatter in some of the reported experiments that determined equilibrium constants for these solids.

Particle size effects may result in a transition in solubility control from one hydrated solid to a dehydrated form as crystal growth occurs. The difference between the Cu(II) dibasic solids CuO(s) and $Cu(OH)_2(s)$ is essentially one water molecule of hydration.[31] The solubility constant determinations (and, therefore, $\Delta G_f^\circ$ determinations), show that at equilibrium, even large particles of cupric hydroxide can never be stable relative to cupric oxide. With smaller particle sizes, the molar surface of the solid phase is correspondingly larger, so there is a point of crystallite size where cupric oxide is thermodynamically unstable relative to the hydroxide.[31,65,66] In practical situations these differences in particle size and solubility could easily change actual equilibrium copper levels by a factor of more than two.

The thermodynamic measurements and arguments do not predict anything about the reaction rates of the conversion and crystal growth of the solids. For example, metastable $\gamma$-FeOOH(s) is known sometimes to take millions of years to convert to the thermodynamically-stable coarse-grained $Fe_2O_3(s)$ in sediments.[31] Reported log $K_{sp}$ values for freshly-precipitated "$Fe(OH)_3$" vary by 3 orders of magnitude.[15]

Adeloju and Hughes suggest that the formation of solid $Cu(OH)_2(s)$ is kinetically favored over the formation of CuO(s) solid.[17] Many researchers have observed significant $Cu(OH)_2(s)$ to be produced by corrosion at anodic locations in electrochemical experiments.[44,45,68-71] These experimental observations, coupled with the levels of copper observed in many sampling programs and pipe rig experimental systems, supplement the argument that at least for relatively new plumbing systems, the use of $Cu(OH)_2(s)$ in the solubility model is more realistic than CuO(s). Metastability may be particularly important for controlling copper in plumbing systems that do not have thick, adherent aged coatings on them.

The transitioning dehydration process from freshly-precipitated, amorphous bluish-green cupric hydroxide, through a brownish color into black CuO has been studied by Patterson, et. al. for alkaline precipitation of copper from dilute cupric nitrate solutions.[72] They found that long-term aging (about a month) experiments corresponded well to the mechanism proposed by Schindler, *et. al.* for growth in crystallite size until cupric oxide became more stable than cupric hydroxide.[65,66]

In assessing the probable accuracy or reliability of solubility constants, one unavoidable interaction is the selection of the stability constants of the background hydrolysis species, eg. $CuOH^+$, $Cu(OH)_2^\circ$, $Cu(OH)_3^-$, etc., used in deriving the solubility constant from experimental data. While other interfering species (such as carbon dioxide, ammonia, chloride) may be excluded from experimental systems, nothing can be done to avoid hydroxide complexes, except operating at low pH. That is clearly not a viable solution for relevant study of oxide and hydroxide solids, because of likely differences in kinetics, surface properties, and speciation differences resulting from high concentrations of metal. As noted previously, Baes and Mesmer indicated problems with several formation constants for cupric hydroxide complexes, and they recommended limiting values for these three complexes, rather than precise numbers.[47] Therefore, only a limited amount of confidence can be placed in the reported $K_{sp}$ for any cupric oxide or hydroxide solid.

## The "Cupric Hydroxide Model"

Using the expression of equation (24), a variety of solubility diagrams were computed using the CU2SOL computer program for 25°C, assuming several concentrations of DIC and different ionic strengths. Initially, the diagrams were computed assuming the free cupric ion activity was fixed by equilibrium with a $Cu(OH)_2$ solid with the highest molar surface (see Tables 1 and 2) by the expression:

$$\left[Cu^{2+}\right]=K'_{s,Cu(OH)_2}\left[H^{+}\right] \qquad \textbf{(27)}$$

in which log $K_{s,Cu(OH)_2}$ was 8.89. Because the maximum ionic strength used in any of the calculations was sufficiently low, the activity of water and of the solid were assumed to be unity for all calculations. The solubility constant for the solid with the highest molar surface was initially chosen for the model because it probably best represents the initial cupric oxide solid formed in the first few months to years of exposure of pure copper pipe to drinking water.

Figure 3 illustrates a three-dimensional surface of the effect of DIC and pH on cupric hydroxide solubility. Alternate selections of solubility constants for $Cu(OH)_2(s)$, or even CuO(s), would yield the same trend, just shifted up or down. To provide a more quantitative estimate of the trends of solubility, a contour diagram was prepared by fitting a grid to copper solubility calculations from DIC 0 to 150 mg C/L and pH 6 to 11, and contouring the interpolated surface, shown in Figure 4. Contour diagrams were constructed using the software packages SigmaPlot® for Windows (2.0) and Surfer® for Windows. The default contouring by SigmaPlot® with logarithmic scaling of intervals was found to be adequately accurate for most purposes, although predicted equilibrium concentrations read from such diagrams should not be considered to be very precise and be overinterpreted. When using some other software, such as Surfer®, careful application of the available grid interpolation and contouring algorithms was necessary, to avoid mathematical artifacts and misleading interpretations of solubility behavior. After some experimentation and hand-checking of computed values from CU2SOL versus those obtained after gridding and contouring, the best results were obtained using the minimum curvature gridding method, a grid size of 101 by 101, normal search method, and a specified maximum error of less than or equal to 0.0005 of the surface relief. A maximum error of ±0.02 in log(mg Cu/L) for some pH values below DIC of 5 mg/L was still found. However, above that DIC, diagram interpolation errors are all less than 0.001 for log(mg Cu/L) for the entire pH range of the figure. Discrepancies between the displayed interpolated values and the raw computed data were somewhat greater for the diagrams with the logarithmic scaling displayed. However, the convenience of the direct reading of concentrations from such diagrams was judged to outweigh the value of the higher display precision, and these diagrams were selected for this report.

An increase in copper solubility with lower pH and higher DIC is evident from the figures. Above a pH of approximately 9.5, an upturn in solubility is predicted, caused by carbonate and hydroxide complexes increasing $Cu(OH)_2(s)$ solubility. In the pH range of approximately 7 to 9, significant increases in copper solubility are predicted from the addition of even small amounts of

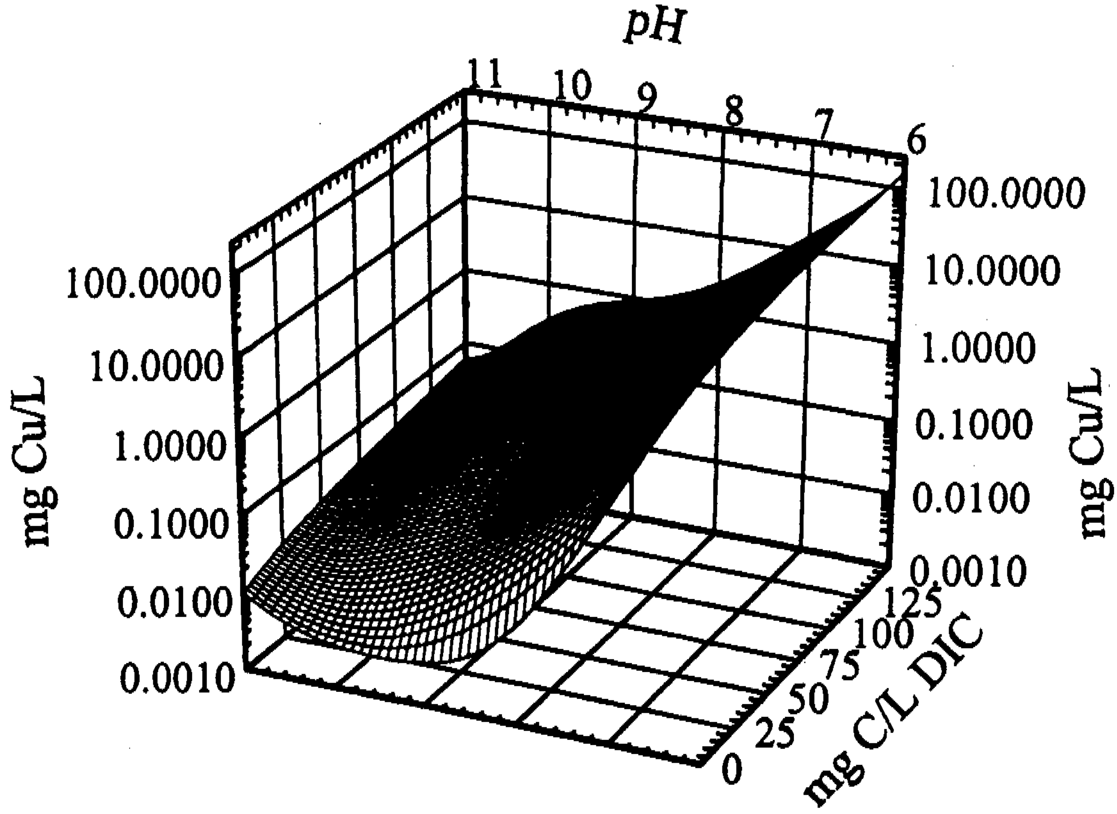


Figure 3. Three-dimensional surface plot of the effect of DIC and pH on copper (II) solubility, assuming equilibrium with $Cu(OH)_2$ having a large molar surface (I=0.02, 25°C).

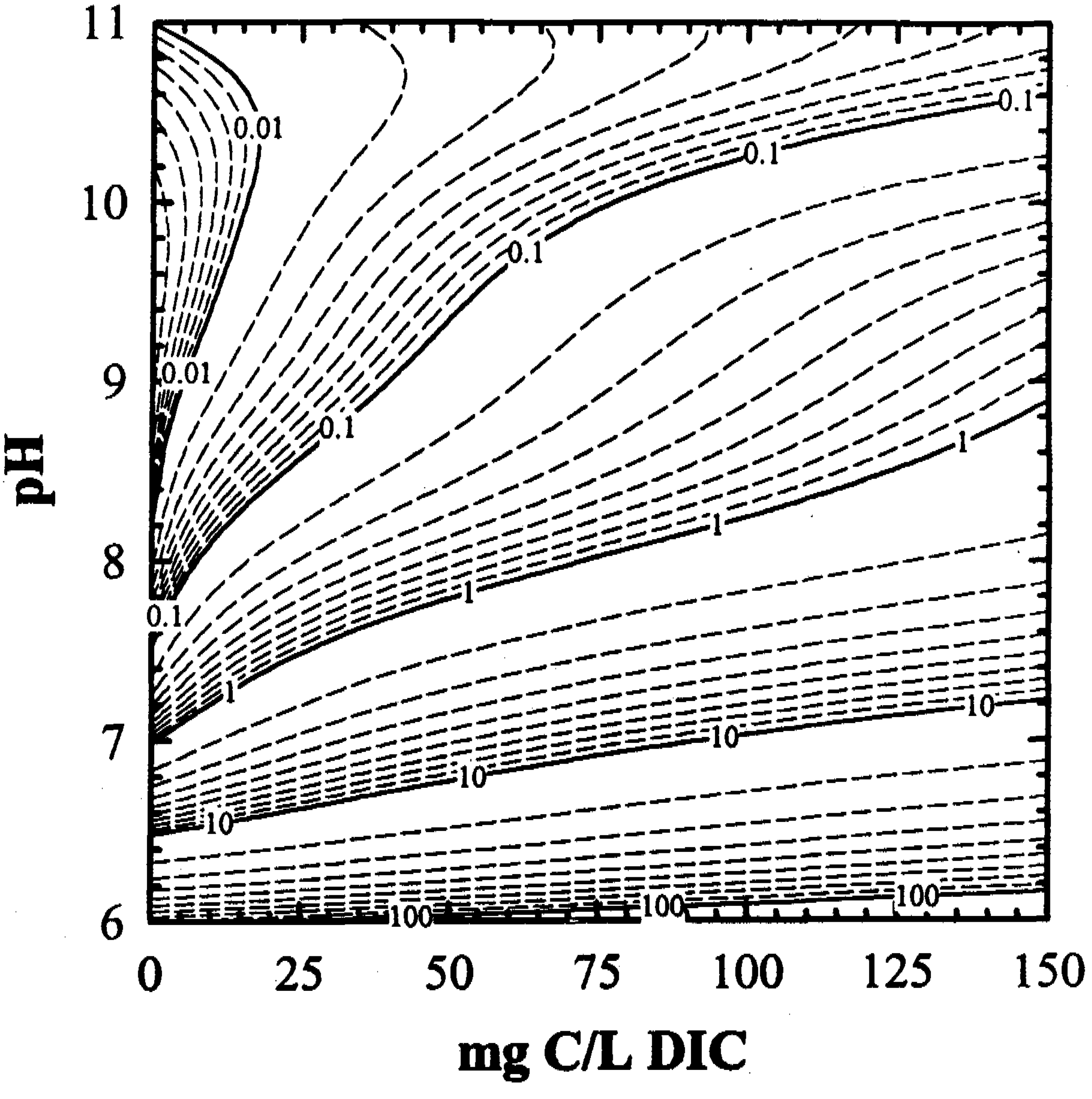


Figure 4. Contour diagram showing the effect of DIC and pH on copper(II) solubility, assuming equilibrium with $Cu(OH)_2$ solid having a large molar surface (I=0.02, 25°C).

carbonate, although maximum solubility remains less than about 0.3 mg/L. The largest relative impact on increasing copper solubility occurs where the contour lines are most nearly parallel to the pH axis, which is in the first approximately 15 mg/L of DIC. The effect remains considerable even above pH 9, but the overall solubility is so low that the enhancement is not of much practical significance.

To understand the roles of the different aqueous species better, Figures 5a and 5b were plotted. These show the predicted aqueous speciation for two concentrations of DIC, 4.8 and 96 mg C/L ($4 \times 10^{-4}$ mol/L and $8 \times 10^{-3}$ mol/L) assuming the formation of the $Cu(OH)_2$ solid with high molar surface.[66] These DIC levels generally represent waters of moderate to very high alkalinity, respectively.

Clearly, carbonate complexation dominates copper(II) solubility in most drinking waters over pH 7, and is the key to developing effective cuprosolvency reduction strategies. In the pH and carbonate concentration ranges of most drinking water, the figures clearly show that complexes with carbonate species are the dominant ones. At a pH of approximately 9.5, the complex $CuCO_3(OH)_2^{2-}$ becomes important in enhancing the solubility of $Cu(OH)_2(s)$. The prediction of increased solubility by waters of increasing DIC is supported by the results of many research and field studies.[73-79]

Computations over the ionic strength range of 0.001 to 0.02 were performed to assess the sensitivity of the solubility calculations to this parameter. Because of the dominance of uncharged aqueous species over much of the pH/DIC range, the effect is generally negligible for practical purposes. At low DIC concentrations and at low pH (eg. DIC=5 mg C/L at pH 6.5) the effect is largest, amounting to approximately 2 mg/L. The impact is rapidly reduced to differences on the order of only one to several parts per billion by pH 8, for all DIC levels checked. The effect is less at higher DIC's because of the prevalence of the $CuCO_3^\circ$ complex.

A study by KIWA tested the impact of several water quality variables on carefully exhumed copper pipe, having well-developed scale layers.[76] They found the maximum stagnation copper levels (CuMAX) were approximately linearly related to DIC, pH and sulfate concentration by the equation

$$CUMAX = 0.52DIC - 1.37pH + 2\left[SO_4^{2-}\right] + 10.2 \qquad \textbf{(28)}$$

in which CUMAX is in mg Cu/L, but DIC and sulfate concentrations are in mmol/L. The signs in the equation show that DIC and sulfate both tend to increase copper solubility, but increased pH significantly reduces solubility. Their finding is in good agreement with the predictions of this model.

## The Malachite Problem

According to previous corrosion and natural water modeling studies, the solid most likely to be controlling the solubility of Cu(II) in drinking water should be the basic cupric carbonate mineral

Figure 5a.

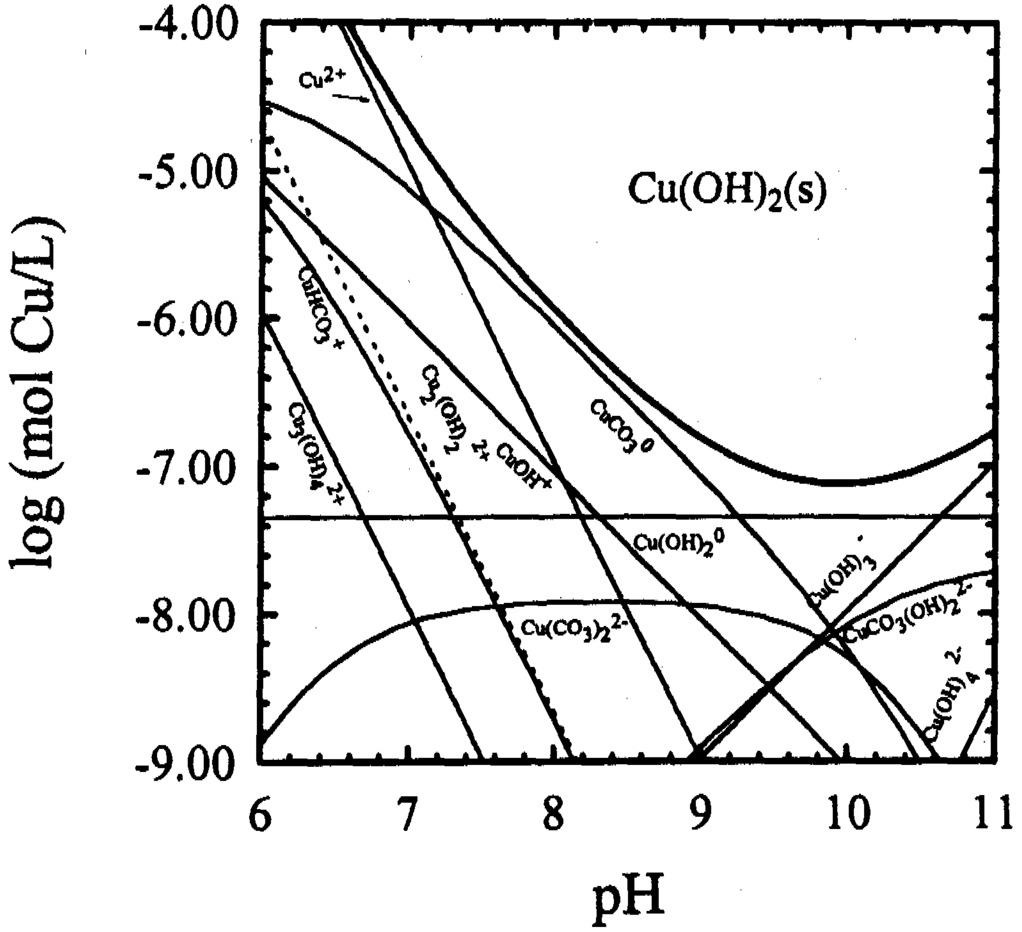
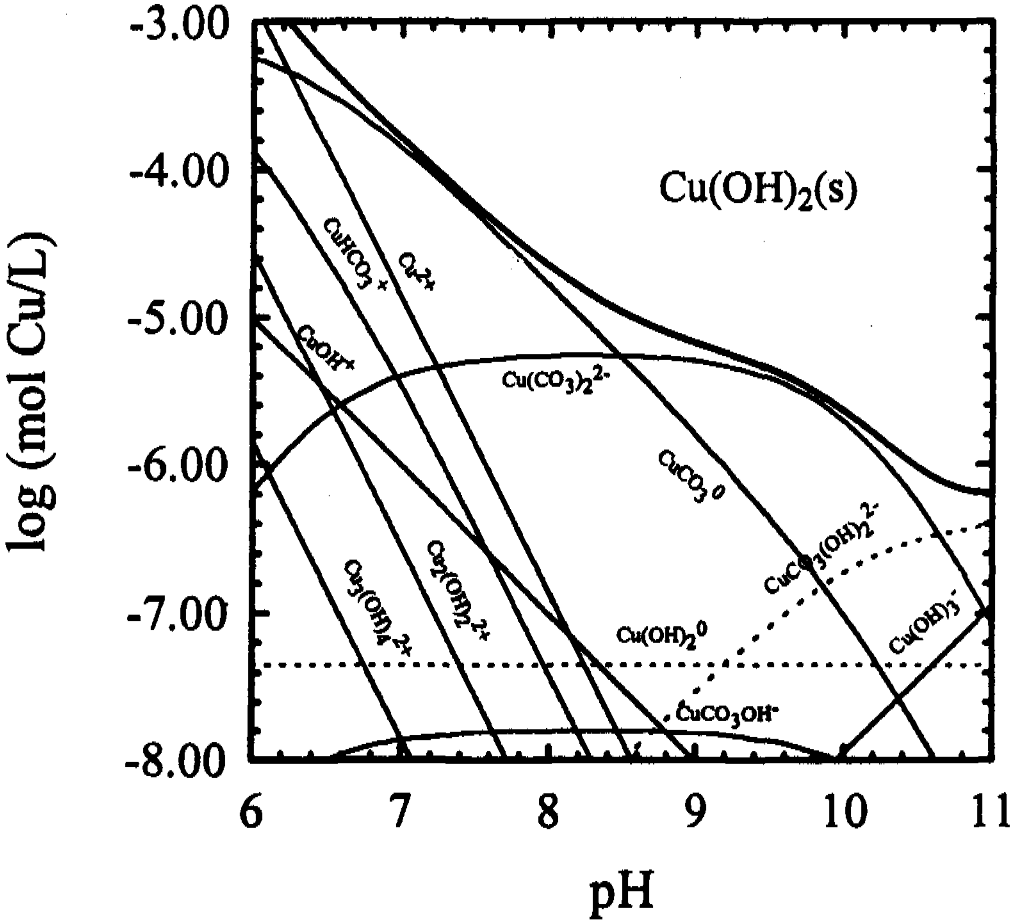


Figure 5. Copper(II) speciation assuming formation of solid $Cu(OH)_2$; a) DIC=4.8 mg C/L I=0.005, 25°C; b) DIC=96 mgC/L, I=0.02, 25°C.

Figure 5b.


-3.00
-4.00
-5.00
-6.00
-7.00
-8.00
log (mol Cu/L)
$Cu(OH)_2(s)$
$CuHCO_3^+$
$Cu^{2+}$
$CuOH^+$
$Cu(CO_3)_2^{2-}$
$CuCO_3^0$
$CuCO_3(OH)_2^{2-}$
$Cu_3(OH)_4^{2+}$
$Cu_2(OH)_2^{2+}$
$Cu(OH)_2^0$
$Cu(OH)_3^-$
$CuCO_3OH^-$
6
7
8
9
10
11
pH

$Cu_2(OH)_2CO_3(s)$ (malachite). Although basic copper chlorides and sulfates, such as langite, posnjakite, brochantite and atacamite may be formed in some circumstances, their significance in uniform corrosion of copper has not been adequately established. Some of these solids, and others like $CuCl_2$, CuCl and $Cu_2(OH)_3Cl$, may be important in pitting processes, however. Complicating the problem is that traditional "eyeball" identification of malachite by its blue-green color is extremely unreliable, because almost all cupric hydroxysulfates, hydroxycarbonates, hydroxychlorides, and even fresh cupric hydroxide can be some shade of blue-green.

There are considerable differences among reported values for the solubility constant of $Cu_2(OH)_2CO_3(s)$ (malachite). For the reaction written as:

$$Cu_2(OH)_2CO_3(s) + 2H^+ \leftrightarrow 2Cu^{2+} + 2H_2O + CO_3{}^{2-} \qquad \textbf{(29)}$$

the most widely-reported values for log K range from -5.16 to -6.20. One study, including some discussion of temperature and redox potential dependence of copper corrosion, used a value that corresponds to -3.99 in the form of equation (29),[17] an extreme difference. The most recent careful experimental work by Symes and Kester[20] leads to a value of log K = -5.48, which has been used for most of the modeling reported here. Little compelling evidence currently exists for the selection of this value over that of Schindler, *et. al.*[80] of -5.18. Thus, the uncertainty in the computed copper concentration in equilibrium with malachite is at least about a factor of 2, aside from uncertainties in aqueous speciation, until further experimental data focusing on this problem is generated.

Figures 6 and 7 show solubility surface and contour diagrams for copper(II), corresponding to equilibrium with either $Cu_2(OH)_2CO_3(s)$ (malachite) or CuO(s) (tenorite), whichever is thermodynamically stable at a given pH/DIC point. These diagrams were constructed in the same manner as Figures 3 and 4. The malachite solubility constant from Symes and Kester was used for both Figures 6 and 7.[20] The solubility constant used for CuO(s) (tenorite) represented the result for the thermodynamically most stable dibasic cupric oxide solid with the smallest molar surface.[66] $Cu_2(OH)_2CO_3$ (malachite) is thermodynamically more stable than any cupric hydroxide or oxide solid in particular pH and DIC ranges. The selection of these two solids was used to provide a simulation of what might happen when recrystallization of cupric hydroxide or slow precipitation of malachite may have taken place over some considerable time. It also provides a representation, for comparison, of the solubility model historically most often applied to drinking water, adjusted for improvements in the understanding of the aqueous speciation of copper(II).

Several important contrasts in cuprosolvency behavior between the case represented by Figures 6 and 7 as opposed to the assumptions behind Figures 3 and 4 should be noted. The "trough" towards the lower pH values and higher DIC values is caused by the $Cu_2(OH)_2CO_3$ (malachite) stability field. If $Cu_2(OH)_2CO_3$ (malachite) is present and capable of forming, below a pH of about 6.5 the addition of DIC is predicted to decrease cuprosolvency, but increase cuprosolvency above about pH 7. There is a small transition zone between these values where the first approximately 5 mg/L of DIC should slightly reduce copper solubility, but additional carbonate would decrease it or have essentially no effect. Below a pH of about 7, equilibrium cuprosolvency becomes essentially insensitive to DIC above approximately 30 mg C/L. Malachite formation would enable attainment

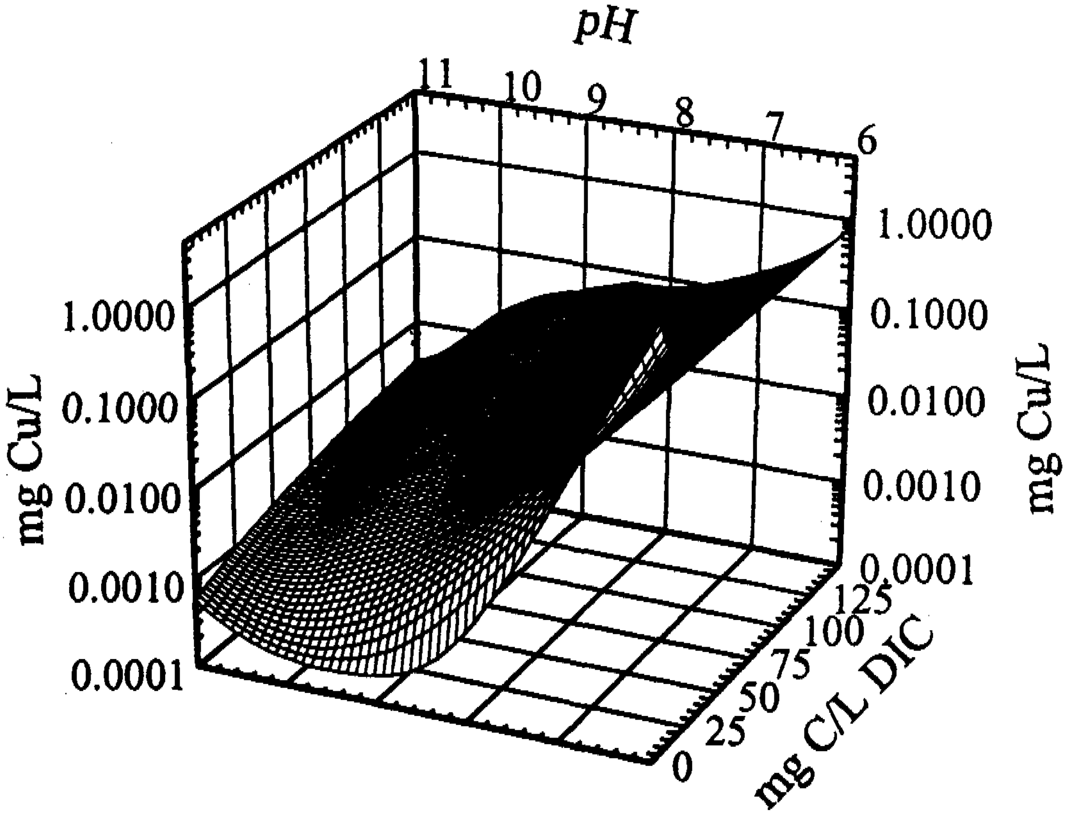


Figure 6. Three-dimensional surface plot of the effect of DIC and pH on copper(II) solubility for aged systems, assuming equilibrium with $Cu_2(OH)_2CO_3$ and CuO (I=0.02, 25°C).

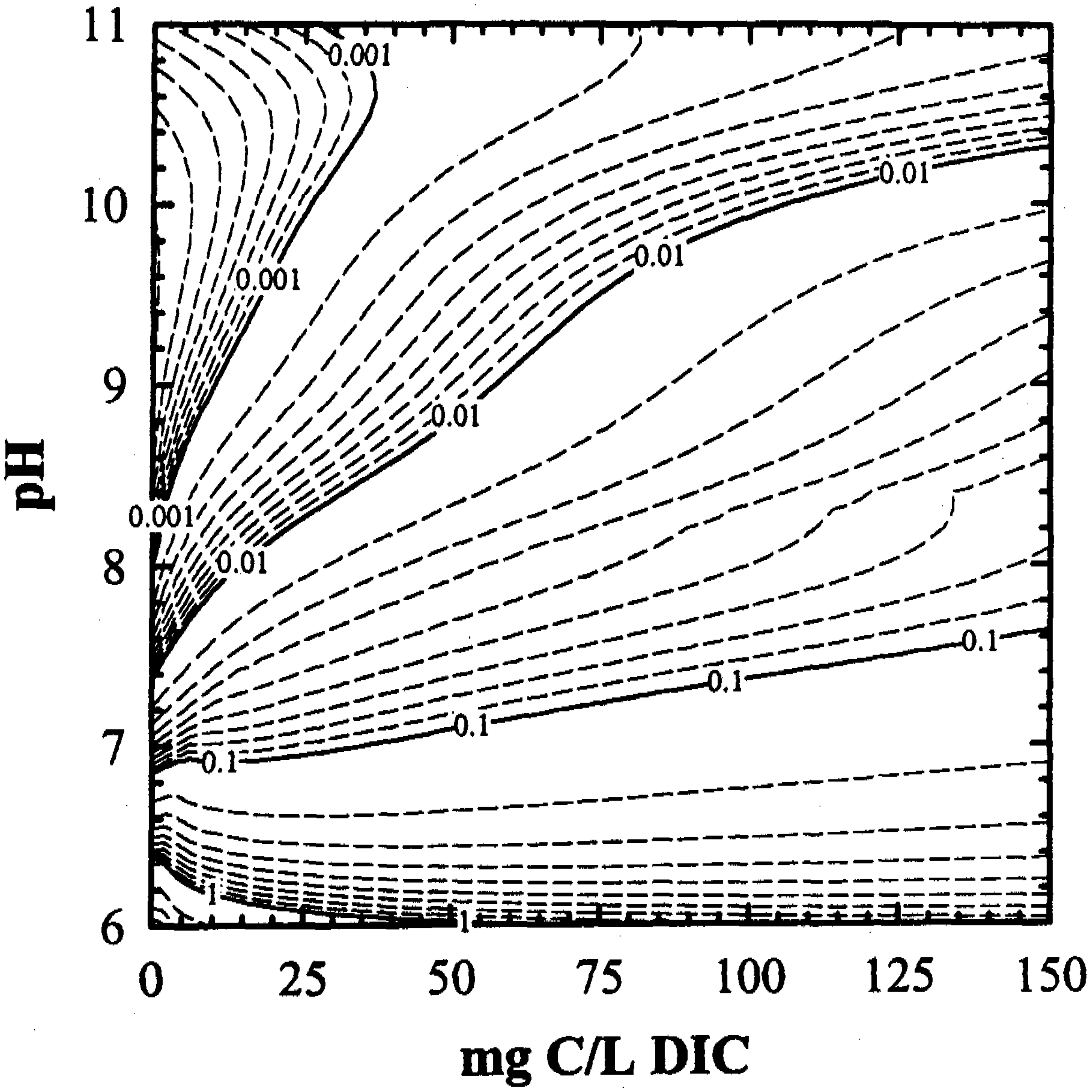


Figure 7. Contour diagram showing the effect of DIC and pH on copper(II) solubility, assuming equilibrium with the stable solid phases $Cu_2(OH)_2CO_3$ (malachite) and CuO (tenorite) at I=0.02 and 25°C.

to the effect of pH and DIC when only cupric hydroxide is formed, where a pH of over 7 would be necessary to stay under 1.3 mg/L for long stagnation times at very low DIC levels, and over 7.5 for systems with high DIC.

Figures 8a and 8b illustrate the impact on predicted copper(II) concentrations produced by some different choices for the solubility constants for $Cu(OH)_2(s)$ (cupric hydroxide) and $Cu_2(OH)_2CO_3(s)$ (malachite). Figure 8a shows that at a fairly low DIC concentration of 4.8 mg C/L ($4.0 \times 10^{-4}$ M) the pH boundary between these two solids can shift from approximately 8.8 to 9.9, depending on the combination of values chosen. At the assumed temperature of 25°C, reasonably representative of normal drinking water temperatures, the impact becomes less as carbonate concentration increases, and the thermodynamic stability domain of $Cu_2(OH)_2CO_3(s)$ (malachite) relative to $Cu(OH)_2(s)$ (cupric hydroxide) widens (Figure 8b). During recrystallization and aging, cupric hydroxide will slowly convert to CuO(s) (tenorite). This will cause the pH of transformation from malachite stability to that of tenorite to occur at lower values than with cupric hydroxide.

In hot water systems the oxide or the hydroxide solid becomes increasingly stable relative to the basic carbonate.[17] The absence of a complete set of formation enthalpies or temperature functions for the various hydroxide and carbonate complexes involved in copper(II) solubility prevent the development of reliable similar diagrams for the 0 to 55°C temperature range of interest to potable water studies.

The previous focus of most copper corrosion research has been on pitting failures and corrosion rate reduction to lengthen the service life of the plumbing systems. Therefore, the significance of malachite formation as a control of copper levels in the first few months or years of service has been given little attention. If malachite formation is kinetically inhibited, or is just relatively slow under normal plumbing usage conditions, the sensitivity of copper solubility to pH will be considerably increased and much higher solubilities are generally expected. This can be seen by examination of Figures 6 and 7, including malachite and tenorite, in contrast with Figures 3 and 4 for cupric hydroxide.

Some evidence for the natural slow formation of malachite has been presented by researchers in different areas. For example, Fruchter, et. al. found that equilibrium with CuO(s) instead of malachite was a much more plausible model for explaining the levels of copper found in fly-ash pore fluids and leachates[81]. From simple mass-action considerations, some increase in the rate of malachite formation with increases in DIC would be highly plausible. However, specific research into the rates of formation of malachite under differenc pH, DIC and flow conditions that would be pertinent to passivation film formation has not been published.

## Effect of Orthophosphate on Copper(II) Solubility

Little information on the solubility of copper orthophosphate solids is available, and almost no progress has been made in identifying solids and determining solubility constants since the absence of reliable thermodynamic data was pointed out in the major review by Rickard in 1970.[51] A tabulation of naturally-occurring copper orthophosphate minerals is given in Table 5.[82] The solid

Figure 8a.

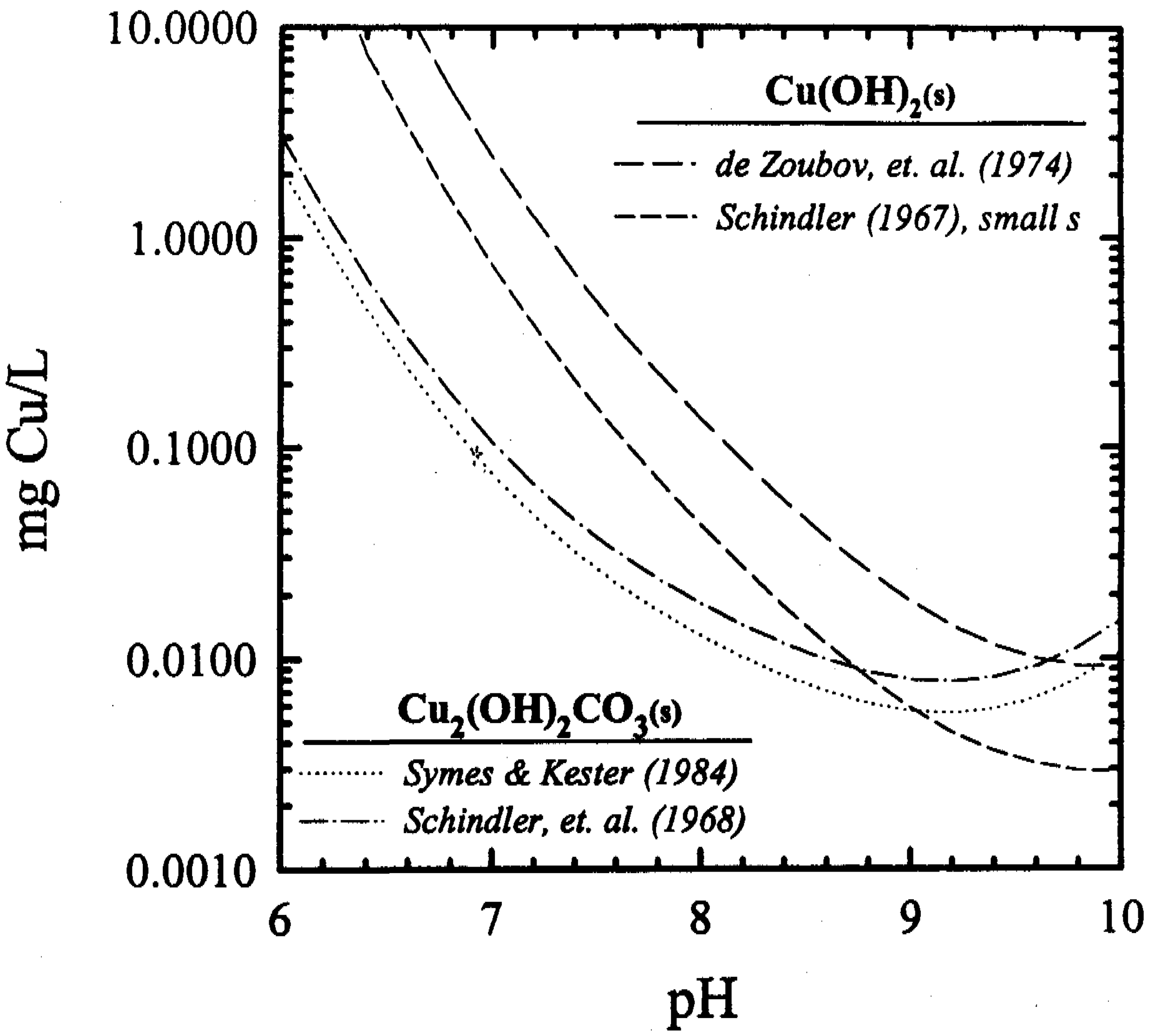
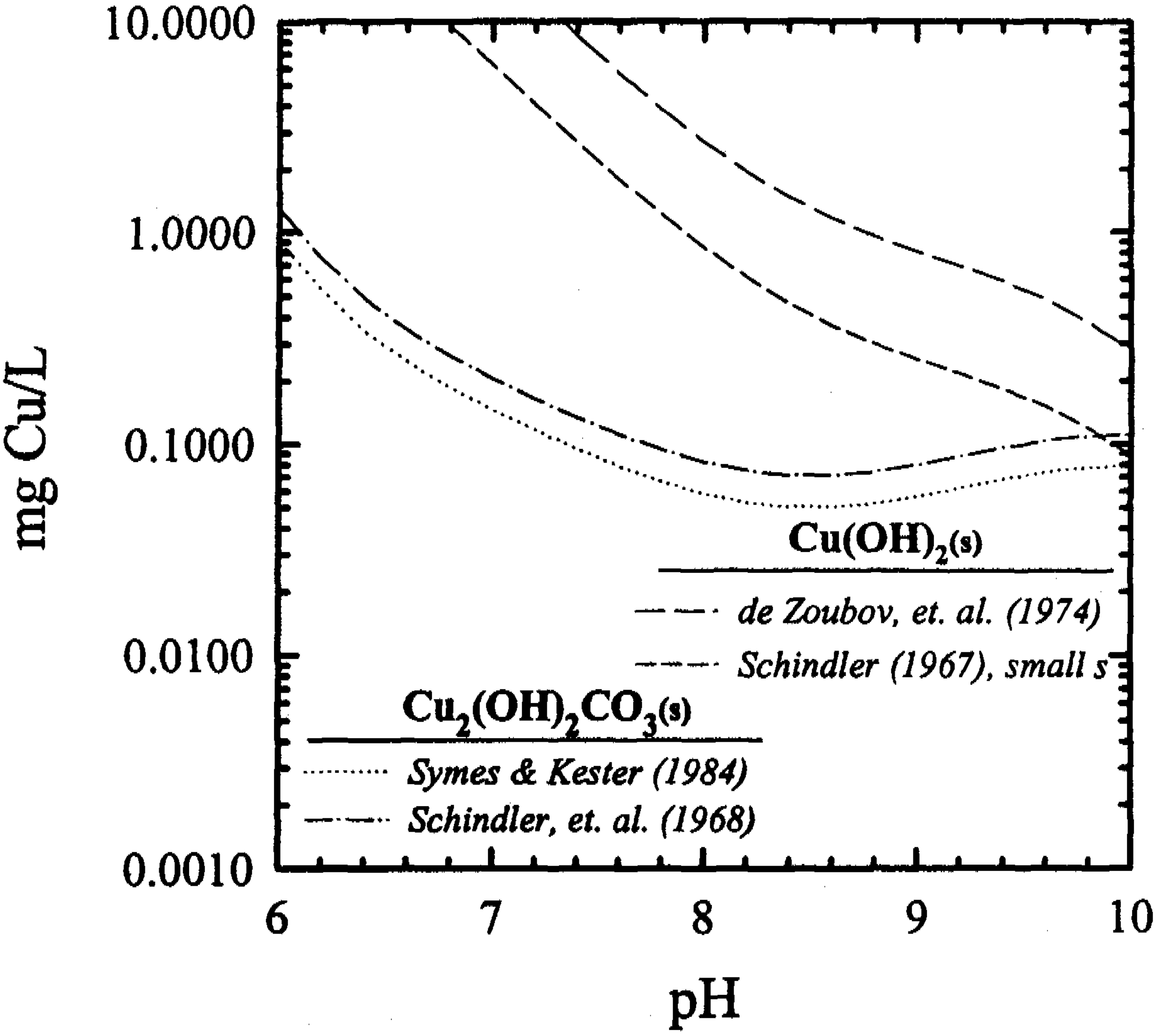


Figure 8. Copper(II) solubility comparison assuming different solids and solubility constants, 25°C; a) DIC = 4.8mg C/L, I=0.005; b) DIC = 96 mg C/L, I=0.02

Figure 8b.


10.0000
1.0000
0.1000
0.0100
0.0010
mg Cu/L
6
7
8
9
10
pH
$Cu(OH)_2(s)$
de Zoubov, et. al. (1974)
Schindler (1967), small s
$Cu_2(OH)_2CO_3(s)$
Symes & Kester (1984)
Schindler, et. al. (1968)

tabulation of naturally-occurring copper orthophosphate minerals is given in Table 5.[82] The solid lebethenite, $Cu_2(PO_4)OH(s)$, has been observed in some hot water copper heat exchanger tube deposits[83]. Unfortunately, no solubility or $\Delta G_f^\circ$ data has been located for any of these minerals. In tabulations of $\Delta G^\circ_f$ data or tables of solubility constants (see Table 1), only the solids $Cu_3(PO_4)_2(s)$ and $Cu_3(PO_4)_2{\cdot}2H_2O(s)$ are listed. Neither of these solids is listed as a naturally-occurring mineral, and their existence in corrosion deposits or passivation films in drinking water pipes is yet to be proven. Because they represent the only solubility estimates available, they are used in these modeling calculations.

**TABLE 5. REPORTED MINERALS CONTAINING COPPER (II) AND ORTHOPHOSPHATE[1]**

| Name | Formula |
|---|---|
| Libethenite | $Cu_2PO_4OH$ |
| Cornetite | $Cu_3PO_4(OH)_3$ |
| Reichenbachite | $Cu_5(PO_4)_2(OH)_4$ |
| Ludjibaite | $Cu_5(PO_4)_2(OH)_4$ |
| Pseudomalachite | $Cu_5(PO_4)_2(OH)_4{\bullet}H_2O$ |
| Nissonite | $Cu_2Mg_2(PO_4)_2(OH)_2{\bullet}5H_2O$ |
| Zapatalite | $Cu_3Al_4(PO_4)_3(OH)_9{\bullet}4H_2O$ |
| Turquoise | $CuAl_4(PO_4)_4(OH)_8{\bullet}5H_2O$ |
| Sieleckite | $Cu_3Al_4(PO_4)_2(OH)_{12}{\bullet}2H_2O$ |
| Planerite | $(Cu,Ca)Al_6(PO_4)_4(OH)_8{\bullet}H_2O$ |
| Hentschelite | $CuFe_2(PO_4)_2(OH)_2$ |
| Andrewsite | $(Cu,Fe^{2+})_3Fe^{3+}{}_6(PO_4)_4(OH)_{12}$ |
| Chalcosiderite | $Cu,Fe^{3+}(PO_4)_4(OH)_8{\bullet}4H_2O$ |
| Phosphofibrite | $KCuFe^{3+}{}_{15}(PO_4)_{12}(OH)_{12}{\bullet}12H_2O$ |

Reference

1. Clark, A.M., *Hey's Mineral Index*. 1993, London: Chapman and Hall.

Orthophosphate has been reported[48] to form two weak complexes with cupric ion, $CuH_2PO_4^+$ and $CuHPO_4^\circ$. The fraction of Cu(II) solublity contributed by orthophosphate complexes is, therefore:

$$S_{Cu(II),PO_4} = \left[CuH_2PO_4^{\ +}\right] + \left[CuHPO_4^{\ \circ}\right] \qquad \textbf{(30)}$$

Substituing appropriate equlibrium constant expressions as before yields the following expression:

$$S_{T,PO_4} = \beta'_{1,2,1}\left[Cu^{2+}\right]\left[H^+\right]^2\left[PO_4^{\ 3-}\right] + \beta'_{1,1,1}\left[Cu^{2+}\right]\left[H^+\right]\left[PO_4^{\ 3-}\right] \qquad \textbf{(31)}$$

When orthophosphate is present, then, the total solubility expression for copper(II) will be:

$$S_{T,Cu(II)} = S_{Cu(II),OH} + S_{Cu(II),CO_3} + S_{Cu(II),PO_4} \qquad \textbf{(32)}$$

Previous modeling calculations with orthophosphate projected a negligible effect[22] or only a small reduction in copper solubility for systems with low carbonate concentrations, and at pH levels around neutral.[84] These predictions resulted from the assumption that $Cu_2(OH)_2CO_3$ (malachite) is the controlling phase for copper levels in the water, as is illustrated in Figure 9.

Two major problems with the solubility data constrain the accuracy of predictions made for orthophosphate effects on copper(II) solubility. First, given little experimental confirmation of the solubility constants, relatively large errors (factor of 2 or more) are conceivable. While the error could be in either direction, if the constants used here are biased high, more benefit in solubility reduction by orthophosphate would be possible in drinking water situations for many water chemistries and chemical dosages. A second scenario is the hypothesis that at least short-term copper levels are controlled by $Cu(OH)_2(s)$, rather than by $Cu_2(OH)_2CO_3(s)$. Then, a very different picture emerges, where the predicted stability field for $Cu_3(PO_4)_2 \cdot 2H_2O(s)$ (the less soluble of the two copper orthophosphates having reported solubility constants) is much larger. This reevaluation is shown in Figures 10a through 10d, representing four different concentrations of DIC and four levels of orthophosphate. Note the extremely important interaction among pH, DIC and orthophosphate concentration in governing both the levels of soluble copper(II), and the pH of minimum solubility.

While the minimum of solubility for the copper orthophosphate solid in waters of low to moderate DIC is indicated to be approximately at pH 7.5 (*eg.* Figures 10a and 10b), progressively larger differences in solubility between the hydroxide and orthophosphate solid occur as pH goes down toward 6. Thus, orthophosphate addition for the control of lead and copper corrosion in a low-DIC water at the frequent target pH of 7.5 will have a significant impact on reducing plumbosolvency, but it may not improve copper control beyond that afforded by raising the pH to 7.5. For water systems not encountering lead material problems, however, doses of orthophosphate at 1-5 mg $PO_4$/L may enable attainment of the 1.3 mg Cu/L action level trigger for copper in new plumbing systems at a pH below the approximately 7.2 to 8 range that otherwise might be necessary for sufficient cuprosolvency reduction. In contrast, for systems in which substantial aging of $Cu(OH)_2(s)$ to $CuO(s)$ has taken place, or in which a substantial film of a $Cu_2(OH)_2CO_3(s)$ (malachite) has developed, orthophosphate addition would not necessarily provide reduction of cuprosolvency (see Figure 9). This phenomenon may explain why some treatments that look promising in pipe loop studies do not work as well when applied to an entire distribution system that has many sites with older copper plumbing.

Two primarily electrochemical and gravimetric studies have shown some reduction in copper corrosion rates by the addition of 1-5 mg $PO_4$/L orthophosphate at pH 7.5 to 8[28,77]. Another study reported reductions in copper concentrations, but the orthophosphate level was approximately 950 mg $PO_4$/L.[85]

The solubility mechanism modeled in this research probably not the only way in which orthophosphate affects cuprosolvency. Other roles orthophosphate might play in copper corrosion could be by causing alteration of the nature or growth rate of passivating films, or the kinetics of oxida-

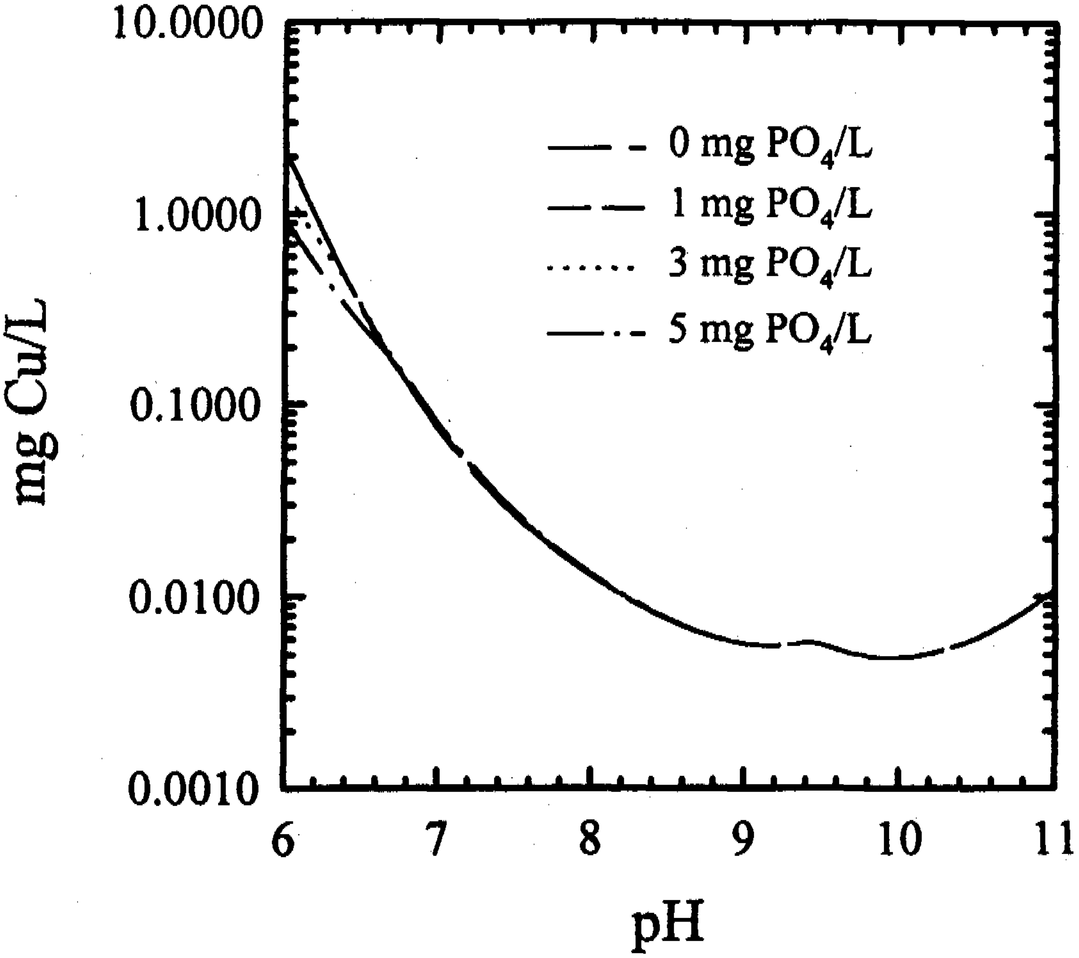


Figure 9. Effect of orthophosphate on copper(II) solubility at DIC = 4.8 mg C/L, I = 0.005 and 25°C, assuming the formation of $Cu(OH)_2(s)$, $Cu_2(OH)_2CO_3(s)$, and $Cu_3(PO_4)_2{\cdot}2H_2O$.

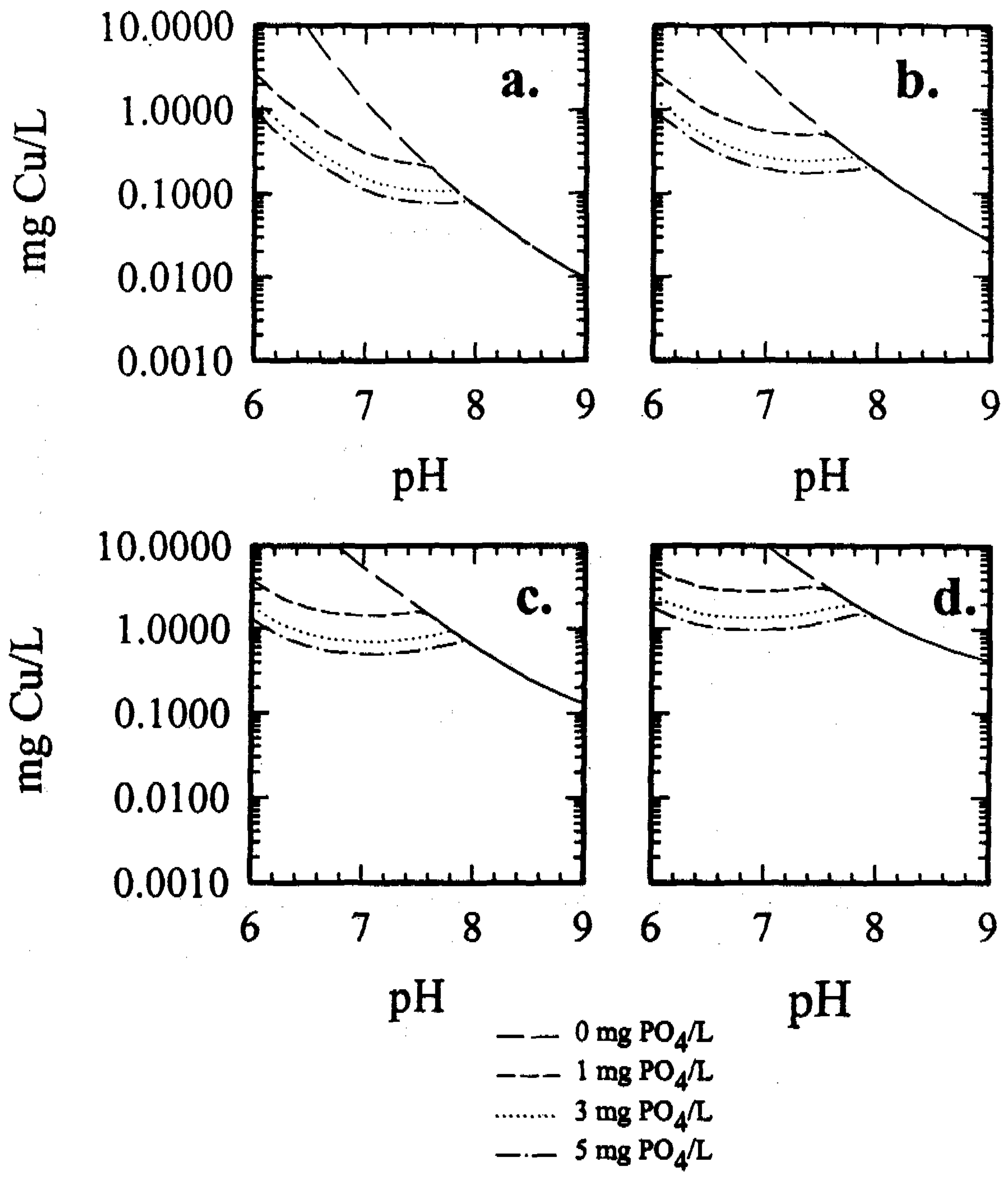


Figure 10. Copper(II) solubility for differenct DIC levels with orthophosphate addition, assuming formation of $Cu(OH)_2(s)$ and $Cu_3(PO_4)_2 \cdot 2H_2O(s)$ at 25°C: a) DIC = 4.8 mg C/L, I = 0.005; b) DIC = 14.4 mg C/L, I = 0.005; c) DIC = 48 mg C/L, I = 0.01; d) DIC = 96 mg C/L, I = 0.02.

phosphate affects cuprosolvency. Other roles orthophosphate might play in copper corrosion could be by causing alteration of the nature or growth rate of passivating films, or the kinetics of oxidation/reduction reactions at the copper pipe surface. For example, visual and X-Ray diffraction of copper pipe surfaces exposed to water with DIC of 5 mg C/L at pH 7, 8, and 9 in ongoing U. S. EPA studies indicate substantial differences in appearance and mineralogy with and without the presence of 3 mg $PO_4$/L orthophosphate. Pipe specimens from the systems having the orthophosphate were almost free of crystalline copper(II) solids. Those experimental systems, as well as identical ones for 10 mg C/L also indicate a drastic reduction in the rate of free chlorine residual depletion in the presence of 3 mg, especially below pH 8. This implies that orthophosphate also plays a critical role somewhere in the oxidation process of copper metal to cupric ion.

A German study has reported 3 mg $PO_4$/L orthophosphate at pH 7.2 and DIC of about 75 mg C/L allows higher copper levels upon stagnation in aged (426-512 days) pipe than without orthophosphate,[84,85] which also indicates that orthophosphate may interfere with the normal corrosion scale oxidation and aging processes. Under some chemical conditions, orthophosphate could preserve higher copper levels that might otherwise be reduced when a stable malachite film formed.

### Effects of Sulfate, Chloride and Ammonia on Copper(II) Solubility

Some minor enhancement of solubility may be produced by the formation of the $CuSO_4^\circ$ aqueous complex in waters of high sulfate concentration, but it is not a very strong complex. At least one value has been reported for a formation constant for a $Cu(SO_4)_2^{2-}$ complex, but its existence remains uncertain. Therefore, aqueous sulfate complexes are not likely to be significant influences on cuprosolvency in potable waters.

Copper forms a wide variety of basic sulfate solids, as are shown in Tables 1 and 2. Only some of the mineral species have either solubility or Gibbs free energy data available for them. The problem is compounded because there is some discrepancy in the X-Ray analysis, mineralogy and thermodynamic data literature on the naming and stoichiometry of some of the solid phases. There is good agreement that the formula $Cu_4(OH)_6SO_4$ applies to the monoclinic mineral brochantite. Hydrated forms of that mineral for which official mineral names exist include: $Cu_4(OH)_6SO_4 \cdot H_2O$ (posnjakite, monoclinic crystal system), $Cu_4(OH)_6SO_4 \cdot 2H_2O$ (langite, orthorhombic crystal system), and $Cu_4(OH)_6SO_4 \cdot 2H_2O$ (wroewolfenite, monoclinic crystal system).[88] Unfortunately, in compilations of Gibbs free energies of formation, the mineral name "langite" is ascribed to $Cu_4(OH)_6SO_4 \cdot H_2O$ by one important primary data source,[89] and to *both* $Cu_4(OH)_6SO_4 \cdot H_2O$ and $Cu_4(OH)_6SO_4 \cdot 1.3H_2O$ by another.[90] Each water of hydration contributes -56.69 kcal to the $\Delta G_f^\circ$ value for the compound, so the computed solubility constant will vary significantly, thus adding confusion to modeling and data analysis.

The kinetic constraints on the formation of these solids in water systems are largely unexplored. Calculations with the CU2SOL model show that even relatively low levels of sulfate (such as 20-30 mg/L) may cause supersaturation of one or more basic cupric sulfate solids in slightly acid to slightly alkaline pH's. Thus, in the pH range of 6 to 8 at low to moderate DIC levels, and in the absence of $Cu_2(OH)_2CO_3$ (malachite) formation, calculations show that basic copper sulfate solids may keep copper solubility below the levels that would otherwise occur through passivation by cupric hydroxide.

Especially above a pH of approximately 8, the persistence of metastable basic cupric sulfate solids when the hydroxide or oxide should be thermodynamically favored is also possible, and is supported by X-Ray analysis in this and other studies.[91] Extensive studies of phase relationships of cupric hydroxide and other precipitates in the presence of sulfate indicated that the ratio of equivalents of cupric sulfate to alkali in a mixture was important in defining the solid produced[92]. For example, if the ratio was equal to or greater than 1.33, the precipitate found was the basic salt $4CuO \cdot SO_3 \cdot 3H_2O$, identical with the mineral brochantite. If the ratio was less than 1, the precipitate was pure cupric hydroxide. Other mixes of solids were found at ratios between 1 and 1.33.

Clearly, some relevence to drinking water plumbing systems is likely. Metastable basic sulfate solids may limit the amount of cuprosolvency reduction possible by pH and DIC adjustment, especially above pH 8. However, a detailed exploration of the solubility ramifications of sulfate is beyond the scope of this investigation, so only various aspects of it are considered where appropriate.

A consensus exists that chloride forms at least three weak complexes with cupric ion, $CuCl^+$, $CuCl_2^\circ$, and $CuCl_3^-$. The complexes $CuOHCl^\circ$ and $Cu_2Cl_4^{2-}$ have also been reported by various researchers, but at typical drinking water concentrations of chloride, they are unlikely to be very significant. Ammonia complexation constants for cupric ion are strong, and the complexes formed are $CuNH_3^{2+}$, $Cu(NH_3)_2^{2+}$, $Cu(NH_3)_3^{2+}$, and $Cu(NH_3)_4^{2+}$. The additional chloride, sulfate and ammonia species of copper(II) may be combined into an additional term, $S_{Cu(II),add}$

$$\begin{aligned} S_{Cu(II),add} = {} & \left[CuCl^+\right]+\left[CuCl_2^\circ\right]+\left[CuCl_3^-\right]+\left[CuSO_4^\circ\right]+\left[CuNH_3^{2+}\right]+ \\ & \left[Cu(NH_3)_2^{2+}\right]+\left[Cu(NH_3)_3^{2+}\right]+\left[Cu(NH_3)_4^{2+}\right] \end{aligned} \quad \textbf{(33)}$$

to complete the copper(II) solubility model as follows.

$$S_{T,Cu(II)} = S_{Cu(II),OH} + S_{Cu(II),CO_3} + S_{Cu(II),PO_4} + S_{Cu(II),add} \quad \textbf{(34)}$$

However, these additional complexes seem to have little predicted effect on overall copper(II) solubility compared to carbonate, which is usually present in much higher concentration than ammonia and chloride. Enhancement of copper solubility during periods of chloramination with considerable excess ammonia present, followed by a decrease in solubility when a period of breakpoint chlorination was practiced was observed for Champaign, IL tap water.[93] Whether this is caused by cuprous ion ammine complexes, cupric ion ammine complexes, or some other mechanism has not been determined.

While some species, such as chloride, dissolved organic materials, and sulfate may not directly enhance equilibrium copper(II) solubility, they may indirectly influence it by modifying the crystal structure, morphology, and compactness of the solids formed at the pipe surface.[79,94,95]

## Interrelationships of Copper(I) and Copper(II)

Figures 11 and 12 are $E_H$-pH (EMF-pH or "Pourbaix") diagrams for systems having relatively low (4.8 mg C/L = 4 x $10^{-4}$M) and relatively high (96 mg C/L = 8 x $10^{-3}$M) levels of dissolved carbonate. For these diagrams, the thermodynamic activities of the aqueous species are assumed to be equal to their concentrations. Aqueous copper species activities are assumed to be at the action level of 1.3 mg Cu/L. Copper(I) solubility is assumed to be controlled by $Cu_2O(s)$ (cuprite). Copper(II) solubility is assumed to be controlled by the metastable $Cu(OH)_2(s)$ high molar surface solid in these figures. These diagrams are in considerable contrast to many published previously, because of the inclusion of the significant cupric carbonate and hydroxycarbonate complexes. The diagrams reflect increasing solubility of copper(II) with DIC.

When transformations from copper(II) to copper(I) are considered, as may take place when oxidizing agents in the water are depleted, an interesting feature emerges. Figure 13a shows solubility curves for copper(II) being controlled by $Cu(OH)_2(s)$ (cupric hydroxide) at three levels of DIC superimposed on solubility curves of the two possible copper(I) solids, $Cu(OH)_2(s)$ and $Cu_2O(s)$ (cuprite). Ammonia and chloride are assumed to be absent. Depending on the pH and DIC levels, major drops in copper solubility could take place after depletion of oxygen and chlorine, as has been suggested by recent research.[86,87] Essentially as an inverse of equation (8), copper metal and cuprous ions in the film layer immediately on the surface of the pipe may serve as reducing agents to convert solution or interstitial cupric ions and fresh cupric hydroxide surficial solids into CuOH(s) (cuprous hydroxide) or $Cu_2O(s)$ (cuprite), by a path such as:

$$Cu(s) + Cu^{2+} \leftrightarrow 2Cu^{+} \tag{35}$$

$$2Cu^{+} + H_2O \leftrightarrow Cu_2O(s) + 2H^{+} \tag{36}$$

The net result of such a reaction process would be a decrease in soluble copper levels as Cu(II) (cupric) aqueous species are reduced to less-soluble Cu(I) (cuprous) forms.

For example, for a DIC of 96 mg/L at pH 8.5, copper solubility could ultimately decrease from about 1 mg/L to a virtually undetectable level (approximately 0.002 mg/L) from this phenomenon. If $Cu_2(OH)_2CO_3$ (malachite) and CuO (tenorite) are the controlling scale-forming solids, as might be the case with aged copper pipe, the concentration change would be much less, as is shown in Figure 13b. Interestingly, the amount of concentration change is predicted to depend on pH and DIC for both newer and older copper surfaces, and whether or not CuOH(s) or $Cu_2O(s)$ (cuprite) most readily forms.

In addition to the cited German research, previous research by Tronstad and Veimo and KIWA indicated the possible occurrence of this effect,[73,76] as has some research in Japan[75]. Thus, copper

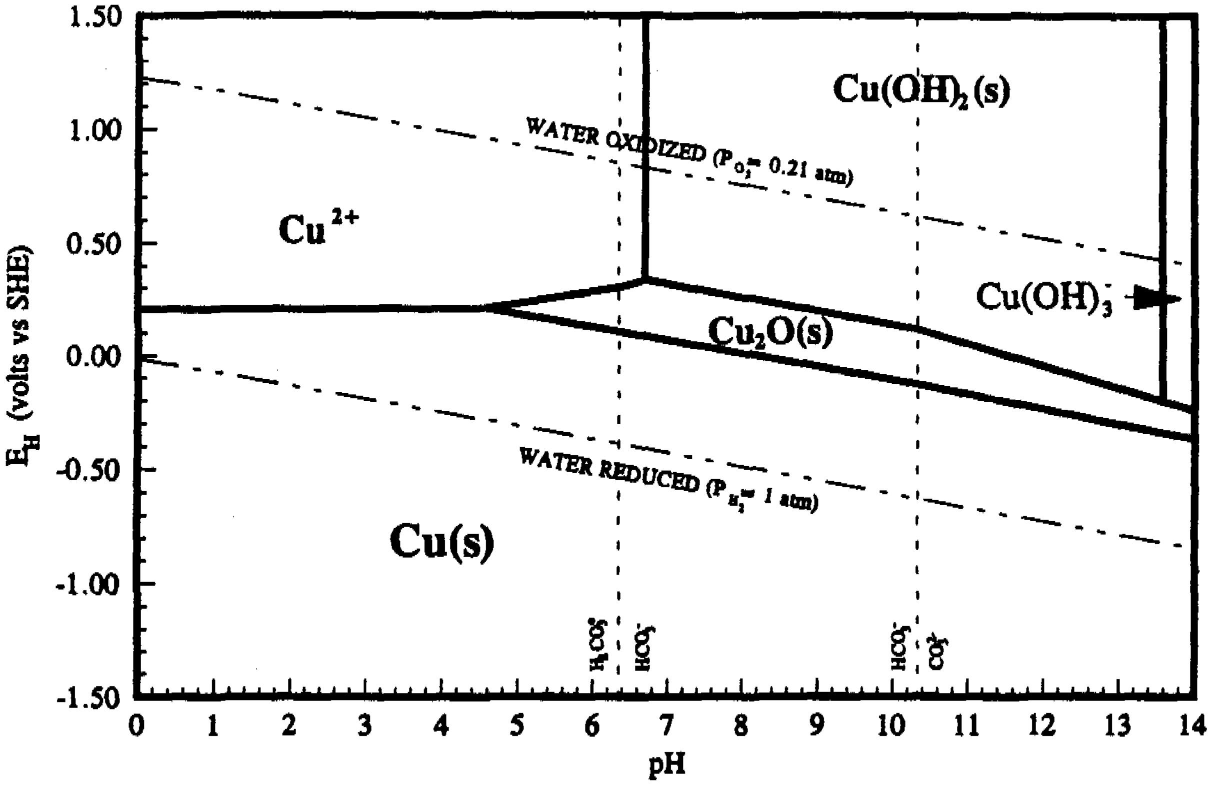


Figure 11. EMF-pH diagram for copper in water containing carbonate, assuming formation of cupric and cuprous hydroxide at DIC = 4.8 mg C/L, I = 0, copper species concentrations of 1.3 mg/L, and 25°C.

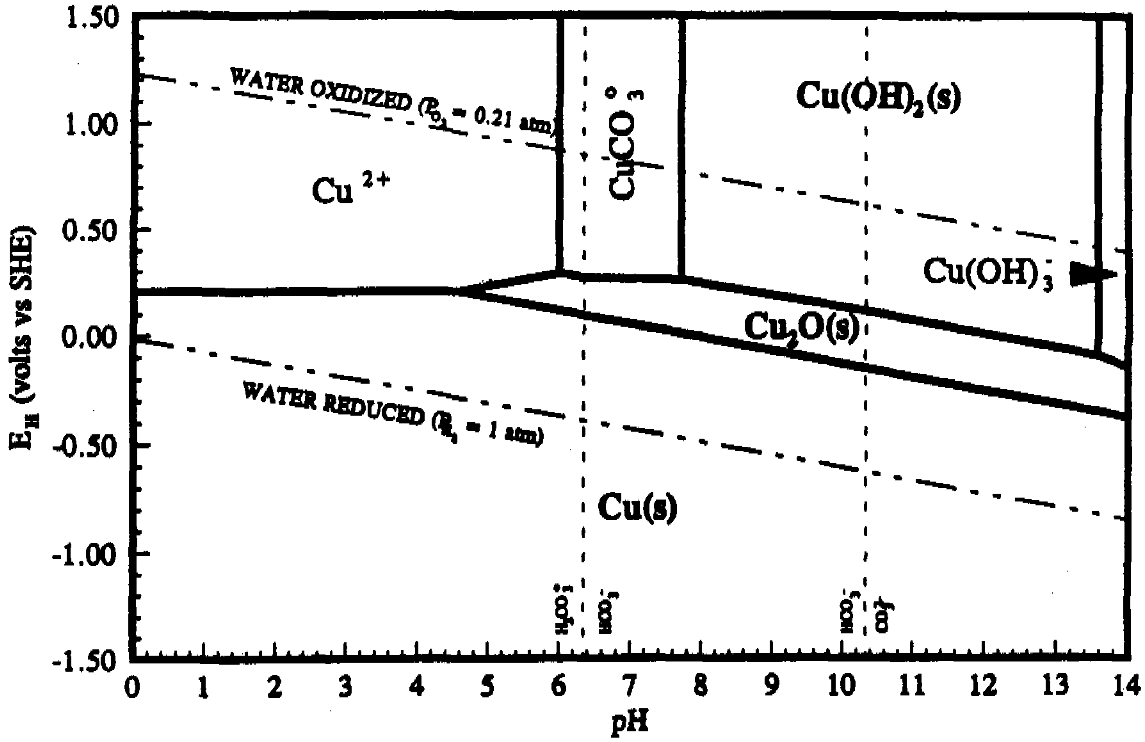


Figure 12. EMF-pH diagram for copper in water containing carbonate, assuming formation of cupric and cuprous hydroxide at DIC = 96 mg C/L, I = 0, copper species concentrations of 1.3 mg/L, and 25°C.

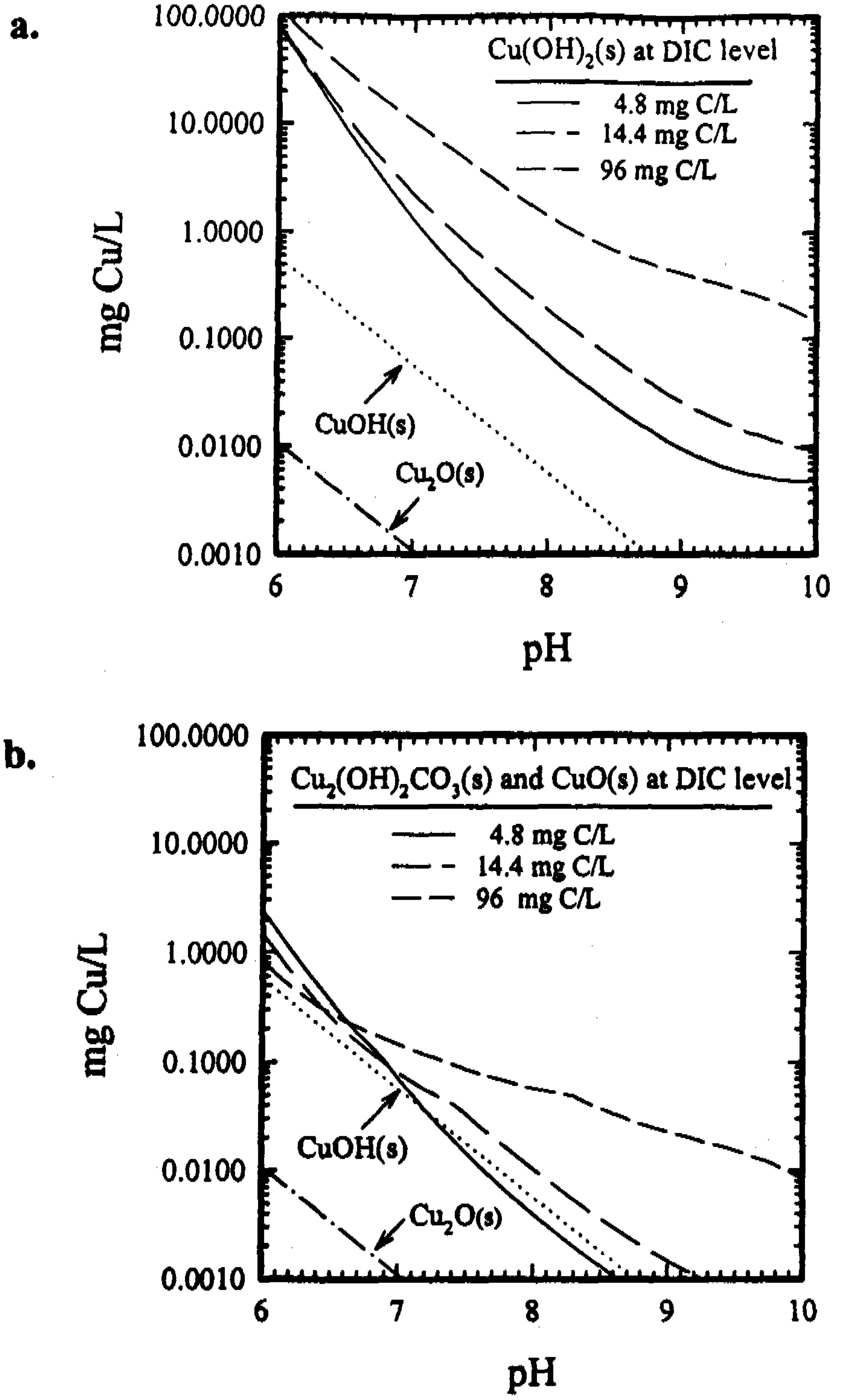


Figure 13. Copper(II) solubility of different DIC levels compared to copper(I) solubility, at I = 0.01, 25°C for: a) newpipe with Cu(OH)$_2$(s); b) aged pipe.

levels at the tap are likely to behave much differently under some chemistry and water usage scenarios than lead (which usually follows classical diffusion-controlled stagnation profiles) when oxidant concentrations are depleted under service conditions. This also has considerable impact on the design and conduct of corrosion optimization studies for copper, both by pipe loop and electrochemical testing. Careful interpretation of the meaning and consistency of standing copper samples must be done, and additional data such as chlorine residual, dissolved oxygen, and other background water chemistry parameters may need to be collected before and after standing in different parts of the distribution system, to enable proper conclusions to be drawn from sampling data.

### *Complications of Dissolved NOM*

Several investigators have looked at interactions between $Cu^{2+}$ and dissolved natural organic matter (NOM). NOM is a diverse collection of material that is mainly composed of humic or fulvic substances, and that is generally characterized empirically by statistical models that describe binding of metals by the formation of one or several theoretical ligands under a specific set of experimental conditions (such as pH and ionic strength). These are numerical constructs that can not always be used for comparison of data for different water supplies or NOM sources. Nonetheless, some features of interaction with copper can be examined.

Some studies suggest that while copper can form complexes with NOM ligands (sometimes called DOM for "dissolved organic matter"), at concentrations of copper typical of drinking waters, copper speciation is more likely dominated by hydrolysis or carbonate complexes.[96-98]

$Cu^{2+}$ ion may also bind with adsorbed organic material containing appropriate functional groups. The binding with adsorbed organic matter seems to be stronger than direct binding with surface sites on several materials tested.[99] Copper present as an organic complex may bind preferentially with adsorbed organic material.[99,100] These studies suggest that some reduction in copper concentration may be caused by adsorbed organic material acting as either a diffusion barrier, or as a less-soluble corrosion film.

Some other studies suggest that NOM may play a major role in the aqueous speciation of cupric ion, particularly when carbonate concentrations are low.[101,102] Organic ligands produced by marine diatoms and during diatom blooms have been shown to strongly complex copper, though usually at low copper concentration.[103,104] Unsaturated organic ligands were also shown in experiments at pHs generally lower than drinking water to increase the dissolution rate of copper metal in the presence of cupric ion, by a complicated interaction affecting the electron transfer rate between Cu(s) and $Cu^{2+}$, and by stabilizing the Cu(I) state by complexation.[105]

The significance of NOM to cuprosolvency relative to drinking water concentrations of copper and competing non-metals and ligands has not been conclusively determined, though it is an area under active investigation by some research groups in the United States. Research into copper plumbing pitting has indicated that some NOM may actually alleviate the propensity of a water to cause pitting attack, and possibly alter some scale formation characteristics of uniform copper corrosion.[91] Any effect on cuprosolvency will likely be stronger in untreated surface water supplies than in ground waters with very low TOC or coagulated and filtered surface waters[106,107,346]. In addition to pH and ionic strength, which have been widely acknowledged to be important in complexation studies with NOM, consideration must also be given to the considerable role that cupric carbonate, hydroxide, and hydroxide/carbonate complexes must play, particularly as the pH increases above 7.

In drinking water systems, the presence of extensive amounts of copper metal piping as a source creates a considerably different environment than natural water or aquifer systems where NOM/copper complexation has been studied most extensively. Further, depending on source water and disinfection conditions, the redox potential of drinking waters can vary over a wider range than natural systems, and a variety and quantity of solids may exist that are also not present in ground waters, lakes and sea water. Because of the uncertainty in the role of NOM, and the lack of availability of routine characterization information and corresponding binding constants, no attempt was made to model its impact in this study. The systems used for confirmation of the solubility model were chosen to be generally free of this complication. Lack of correspondence between cuprosolvency predictions and appropriately chosen field water samples may be at least partly the result of NOM effects, and that should be borne in mind when data is evaluated.

# Experimental and Field Evidence for the "Cupric Hydroxide Model"

## Experimental Systems

### *Analytical and Data Reporting Procedures*

Chemical analytical procedures used by DWRD for the experiments used in this report are listed in Table 6, along with the observed detection limits. Because the experiments described in this report took place over several years, there were some changes in analysis procedures over that time. The analysis of most metals was switched from a flame atomic absorption spectroscopy (AAS) system to a simultaneous inductively-coupled plasma spectroscopy (ICP) system during August 1993, after comparability was statistically established. This change also improved the detection limits and low-level precision for the copper analyses. Potassium was always determined by flame AAS, and low-level lead determinations were always done by matrix-modified graphite furnace AAS. The analysis of Si by ICP (reported as $SiO_2$) was substituted for the automated colorimetric silicate procedure in November, 1993. The analysis of total sulfur by ICP replaced the automated turbidimetric procedure in January, 1994. This was primarily implemented to reduce the analyst workload and improve analytical throughput, rather than to improve the accuracy of the analysis. Because the presence of sulfide or other reduced sulfur species is chemically impossible or the concentrations negligible in DWRD experiments, for all calculations the ICP analysis of total sulfur is interpreted as sulfate.

The pH measurement procedure for the laboratory experiments followed the closed-system technique previously developed at EPA.[108,109] Triplicate samples were carefully collected in 15 mL glass vials, which were sealed with no air space by caps having conical polyethylene liners until analysis. The measurement process was made more precise and accurate by linking the pH meter output to a personal computer through an RS-232 port, and monitoring stabilization through a BASIC program. A sample pH was considered stable when three successive 10-second measurements showed an estimated standard deviation of less than 0.001 pH. Standardization of the pH meter was accomplished either directly with pH buffers obtained from NIST[†], or with commercially-prepared buffers accurate to within 0.005 pH that were directly traceable to NIST buffers. Samples were analyzed at least in triplicate. The final pH almost always reflects replication of the final two samples to within ± 0.01 pH.

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[†] National Institute of Standards and Technology, Gaithersburg, MD.

### TABLE 6. ANALYTICAL METHODS USED FOR CHEMICAL ANALYSIS OF WATER SAMPLES

| Analysis | Method | Method Number | Reference | Detection Limit (mg/L) |
|---|---|---|---|---|
| Metals | | | | |
| Calcium | AA-Flame | 7140 | EPA[1] | 0.1 |
| Magnesium | AA-Flame | 7450 | EPA[1] | 2.0 |
| Sodium | AA-Flame | 7770 | EPA[1] | 3.0 |
| Potassium | AA-Flame | 7610 | EPA[1] | 0.25 |
| Iron | AA-Flame | 7380 | EPA[1] | 0.05 |
| Copper | AA-Flame | 7210 | EPA[1] | 0.02 |
| Lead | GFAAS | 7421 | EPA[1] | 0.002 |
| Zinc | AA-Flame | 7950 | EPA[1] | 0.01 |
| Manganese | AA-Flame | 7460 | EPA[1] | 0.01 |
| Calcium | ICAP | 200.7 | EPA[2] | 0.01 |
| Magnesium | ICAP | 200.7 | EPA[2] | 0.025 |
| Sodium | ICAP | 200.7 | EPA[2] | 0.025 |
| Copper | ICAP | 200.7 | EPA[2] | 0.003 |
| Lead | ICAP | 200.7 | EPA[2] | 0.02 |
| Zinc | ICAP | 200.7 | EPA[2] | 0.001 |
| Manganese | ICAP | 200.7 | EPA[2] | 0.0004 |
| Silicon (as $SiO_2$) | ICAP | 200.7 | EPA[2] | 0.053 |
| Sulfur (as $SO_4$) | ICAP | 200.7 | EPA[2] | 0.045 |
| Aluminum | ICAP | 200.7 | EPA[2] | 0.025 |
| Iron | ICAP | 200.7 | EPA[2] | 0.002 |
| Anions | | | | |
| Chloride | Automated Potentiometric Titration | 4500-$Cl^-$ D. | Std. Methods[3] | 1.0 |
| Fluoride | Automated Standard Additons | — | Orion[4] | <0.1 |
| | Potentiometric ISE | 340.2 | EPA[5] | 0.10 |
| Orthophosphate | Automated Colorimetric | I-2601-85 | USGS[6] | 0.02 (as $PO_4$) |
| Total Phosphate | Automated Colorimetric | I-2600-85 | USGS[6] | 0.05 (as $PO_4$) |
| Nitrate -N | Automated Colorimetric | A303-5173-00 | Alpkem[7] | 0.02 (as N) |
| Silicate | Automated Colorimetric | A303-5220-13 | Alpkem[7] | 0.4 (as $SiO_2$) |
| Sulfate | Automated Turbidimetric | A303-5220 | Alpkem[7] | ~6.0 (as $SO_4$) |
| Total Alkalinity | Automated Potentiometric Titration to Equivalence Point | 2320 B.4.6. | Std. Methods[3] | ~0.3 (as $CaCO_3$) |
| Others | | | | |
| Dissolved Oxygen | Winkler (Azide Modification) | 4500-0 D. | Std. Methods[3] | 0.50 |
| Ammonia | Automated Colorimetric | 350.1 | EPA[5] | 0.03 |
| Total Inorganic Carbon | Coulometric Titration | D513-92 | ASTM[8] | < 0.5 |
| Total Chlorine | DPD Colorimetric | 8167 | Hach[9] | 0.02 |
| Free Chlorine | DPD Colorimetric | 8021 | Hach[9] | 0.02 |
| pH | Closed-System Electrometric | — | EPA (DWRD)[10] | — |

[1] RREL SW846, Sept. 1986.

[2] USEPA, "Methods for the Determination of Metals in Environmental Samples," EPA-600/4-91-010 (1994).

[3] "Standard Methods for the Examination of Water and Wastewater," 18th Edition (1992).

[4] Orion Research, Inc., Boston, MA.

[5] USEPA, "Methods for Chemical Analysis of Water and Wastes," EPA-60014-79-020 (1983).

[6] Modified from methods for Determination of Inorganic Substances in Water & Fluvial Sediments, U.S. Geological Survey Open-File Report, (85-495) 1985.

[7] Alpkem Research, Inc., Clackamas, OR.

[8] "1994 Annual Book of ASTM Standards," section 11, volume 11.01 Water (I).

[9] Hach Company, Loveland, CO.

[10] Drinking Water Research Division, USEPA, Internal Method. References: *Journal AWWA* 72:5:304 (1980); Schock & Lytle, *Proc. AWWA WQTC* (1994).

For the recirculation solubility and late runs of the coupon study experiments, DIC was analyzed directly using a coulometric method.[110] This has frequently been found to be more accurate and precise than deriving the concentration from two measured quantities (pH and total alkalinity), each with an analytical uncertainty. The combined method and sampling standard deviation for

DIC during the course of this study was computed using pooled data from analyses of duplicate samples, and was determined to be ±0.1 mg C/L, with no statistically-significant concentration dependence over the experimental range of 5 to 70 mg C/L.

Quality assurance practices for the instrumental analyses followed the usual documented Inorganics and Particulates Control Branch standard operating procedures, that include requirements for analysis of duplicates and spikes of samples comprising more than 10% of the sample load, and verification of instrument calibration and some interference checking through external certified reference standards at multiple times during each analytical run. The exact location and frequency of different types of quality control spikes, standards, blanks, and duplicates, along with accuracy requirements, are specified in those documented procedures for each type of analysis. They cannot be generalized because the precision and accuracy expectations vary with the type of instrument used and the levels of the analyte encountered in the different experiments.

One general indicator of the completeness and accuracy of the analyses performed in each experiment is a check of the percent ion balance error.[111] Computations of ion balance errors on all samples used in the computation of Saturation Indices and which were used for solubility model evaluation were made using fully speciated results from the WATEQX model[112]. These calculations are summarized in box plot form in Figure 14. The analyses are shown to be extremely complete, and the biases well below ± 5% for almost all analyses for all three DWRD studies covered in this report.

Data reporting for tabulations and statistical evaluation followed the recommendations of the ASTM standard practice for low-level data (D4210-83).[113] In this practice, actual instrument results, including negative values, are reported and used in statistical calculations, to avoid inaccuracies brought about by artificial data truncation commonly used by environmental laboratories. After computations and statistical summaries were completed, concentrations below observed analytical detection limits were replaced by the detection limit. When analytical procedures were changed during an experimental run, the most conservative method detection limit that was applicable during that run was used in the tabulation.

X-Ray diffraction analysis was performed on corrosion deposits from pipe samples, whenever sufficient sample volume was available. Deposits scraped from the pipe sections were finely ground by synthetic ruby or agate mortar and pestle, to pass through a 200-mesh sieve (approximately 75 µm) whenever possible. Samples were then suspended as a slurry with amyl acetate, and deposited on zero-background quartz plates by disposable pipettes for mounting in the powder diffractometer.

The instrument used was a Scintag XDS-2000 theta-theta diffractometer with a copper X-Ray tube operated at 45 kV and 33 mA. Scans were usually over the range of 5 to 60 degrees 2-theta, with 0.03 degree step sizes that were held for 3 seconds each. Pattern analysis, performed with the software provided by the instrument manuacturer, generally followed procedures outlined by ASTM.[114]

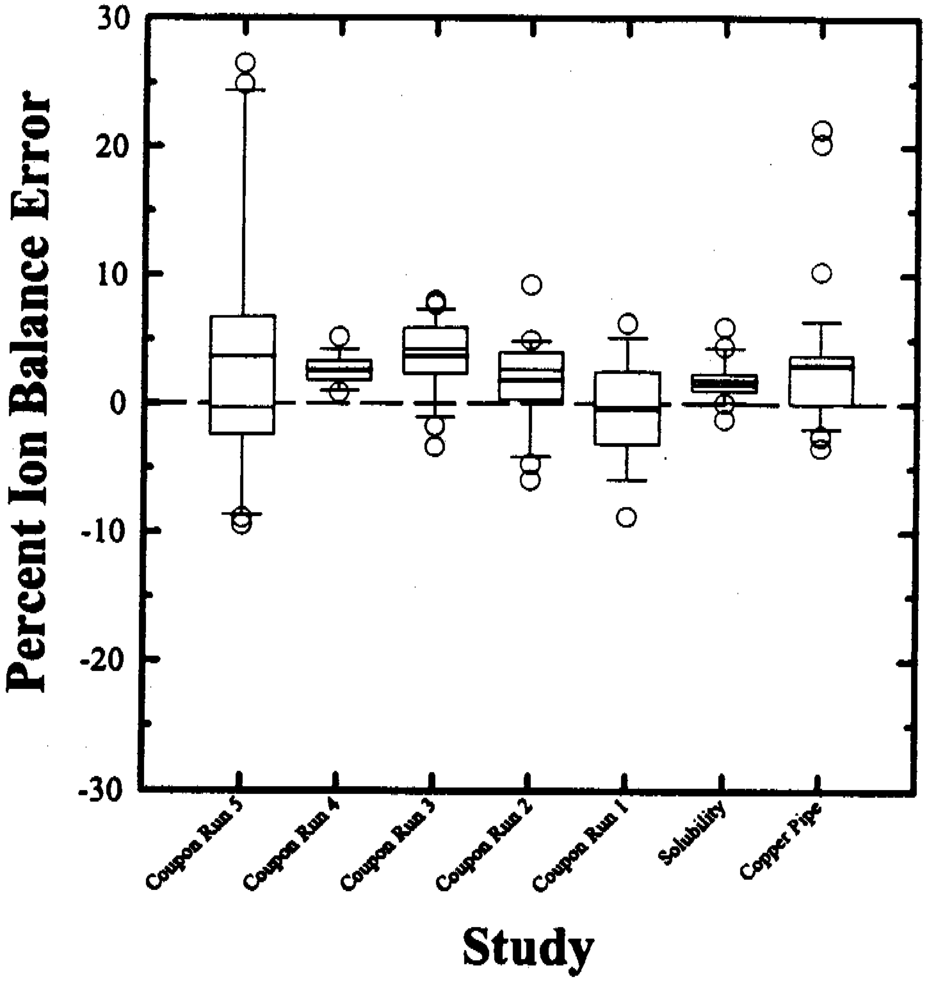

Figure 14. Box plots of percent ion balance errors for complete water analyses from the laboratory experimental runs reported. Boxes show mean (dark line), median (light line), 25th and 75th percentiles (box borders), and the 10th and 90th percentiles (error bars). Data outside these limits are marked (open circles). Large errors represent missing analytes.

### *Coupon Experiments*

Even though the experiments were not designed for this purpose, relevent data for copper corrosion was obtained from a multi-year evaluation of the effect of pH, orthophosphate concentration and metal composition (eg. lead percentage) on the leaching of metals from brass in Cincinnati tap water.[115] In the study, "control" coupons of pure copper (CDA 122) were included in the investigation. The basic test system consisted of a 100 gallon (379 L) heavy-gauge polyethylene reservoir tank with a floating lid, that fed a manifold of 12 30-mL teflon™ cells containing standardized 1-in x 2-in x 0.125-in (2.5-cm x 5.1-cm x 0.32-cm) metal coupons[†]. Coupons were cleaned using a procedure devised to remove cross-contamination from manufacturing, plus chemically cleaning the surface, to assure uniformity of behavior.[115] Chemical cleaning steps used a surfactant soak, a brief 30% HCl soak, and a final acetone rinse. Between cleaning steps, speicmens were thoroughtly rinsed with ultra-pure deionized water.

A pump containing a non-metallic chamber fed the system with test water through all PVC plastic and teflon™ tubing. Rotameters and needle valves were used to adjust the flow rates for uniformity. Teflon™ three-way valves were used to allow draining of the cells for daily water exchange or sampling.

In the first several experimental runs, the reservoir tank was filled daily from the tap water source. The pH was adjusted by manually dosing the tank water with 6 N HCl or 8 N NaOH. When orthophosphate was tested, it was checked daily and adjusted if necessary by dosing with a standardized solution of 0.1 M $Na_2HPO_4$. The water quality in the tank was found to be chemically stable enough in later runs that the tank only had to be refilled one time per week. However, the free chlorine residual and pH were checked daily and adjusted to meet target values, if necessary. In all experiments, water chemistry samples were taken from the reservoir daily to provide a background characterization of the water quality.

Each day, water was drained from all cells, and the manifold cells were flushed with a total of approximately 10 gallons (38 L) of reservoir water, corresponding to approximately 0.8 gallons (3 L) per cell. At the beginning of the runs, samples from each cell were collected daily for analysis. During later run stages, cells were sampled 2 to 3 times per week. Standing times for the coupons were 24 hours during the week, and 72 hours over the weekend. Because of the limited cell volume and air contact during sample collection, sensitive parameters such as pH, chlorine residual and dissolved oxygen could not be analyzed on these stagnation samples. Sample volume was also inadequate to enable estimation of dissolved versus colloidal or particulate material by filtration.

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[†] Metal Samples, Inc., Munford, Alabama.

The five experiments (Runs 1-5 in subsequent discussions) covered the following conditions.

1. The effect of the background tap water distributed by the Cincinnati Water Works Richard Miller Water Treatment Plant (California, OH), with an unadjusted pH of approximately 8.5;
2. The effect of the same background tap water quality, but at pH adjusted to 7.
3. The effect of 3 mg $PO_4$/L disodium orthophosphate at pH adjusted to 7.5.
4. The effect of 0.5 mg $PO_4$/L disodium orthophosphate at pH adjusted to 7.5; and,
5. The effect of background tap water quality with pH adjusted to 7.5.

The background water qualities for each run of this "Coupon Study" are summarized in Table 7. Note that several chemical constituents fluctuated widely over the course of some of the individual runs, and from one run to another. Inability to maintain a constant background water chemistry to isolate the most significant chemical variables put some important contraints on the ability to use data from this experimental study to confirm the accuracy of the solubility model.

**TABLE 7. SUMMARY STATISTICS FOR THE VARIATION IN BACKGROUND WATER QUALITY DURING THE DIFFERENT RUNS OF THE COUPON CORROSION STUDY**

Run #1

| Analyte | N | Min | Max | Mean | Std. Dev. | 95% CI | Median |
|---|---|---|---|---|---|---|---|
| Lead, µg/L | 70 | <0.002 | 11.9 | 1.4 | 2.4 | 0.7 | 0.48 |
| Calcium, mg/L | 64 | 34.7 | 54.8 | 42.4 | 4.6 | 1.2 | 40.9 |
| Copper, mg/L | 54 | <0.02 | 0.03 | 0.00 | <0.02 | <0.02 | <0.02 |
| Iron, mg/L | 57 | <0.05 | 0.07 | <0.05 | <0.05 | <0.05 | <0.05 |
| Potassium, mg/L | 54 | 2.3 | 4.4 | 3.5 | 0.45 | 0.5 | 3.6 |
| Magnesium, mg/L | 64 | 9.1 | 016.6 | 13.5 | 1.8 | 0.5 | 13.5 |
| Manganese, mg/L | 43 | <0.01 | 0.03 | <0.01 | 0.01 | 0.01 | <0.01 |
| Sodium, mg/L | 64 | 14.8 | 44.5 | 33.4 | 6.8 | 1.8 | 34.7 |
| Zinc, mg/L | 58 | <0.01 | 0.39 | 0.03 | 0.06 | 0.02 | 0.01 |
| Alkalinity, mg $CaCO_3$/L | 60 | 43.5 | 74.1 | 60.2 | 5.6 | 1.4 | 60.4 |
| Sulfate, mg $SO_4$/L | 46 | 104.0 | 130.0 | 116.3 | 7.9 | 2.3 | 115.0 |
| Chloride, mg/L | 32 | 39.0 | 43.8 | 40.3 | 1.2 | 0.4 | 39.9 |
| Silica, mg $SiO_2$/L | 5 | 2.4 | 2.8 | 2.6 | 0.2 | 0.3 | 2.8 |
| Nitrate, mg N/L | 54 | <0.02 | 1.1 | 0.77 | 0.17 | 0.04 | 0.73 |
| Ammonia, mg N/L | 54 | <0.03 | <0.03 | <0.03 | 0.00 | 0.00 | <0.03 |
| Orthophosphate, mg $PO_4$/L | 25 | <0.02 | 0.37 | <0.02 | 0.08 | 0.08 | <0.02 |
| Dissolved oxygen, mg/L | na* | na* | na* | na* | na* | na* | na* |
| Total inorganic carbon, mg C/L | na* | na* | na* | na* | na* | na* | na* |
| Free chlorine, mg $Cl_2$/L | 68 | 0.65 | 3.1 | 2.0 | 0.56 | 0.14 | 2.00 |
| pH, pH units | 67 | 8.04 | 8.79 | 8.53 | 0.18 | 0.04 | 8.54 |

*na = not analyzed

Run #2

| Analyte | N | Min | Max | Mean | Std. Dev. | 95% CI | Median |
|---|---|---|---|---|---|---|---|
| Lead, µg/L | 93 | <0.002 | 14.1 | 0.68 | 2.12 | 0.44 | 0.50 |
| Calcium, mg/L | 91 | 25.6 | 51.2 | 33.5 | 6.3 | 1.3 | 33.3 |
| Copper, mg/L | 90 | <0.02 | 2.3 | 0.05 | 0.37 | 0.08 | <0.02 |
| Iron, mg/L | 89 | <0.05 | 0.66 | <0.05 | 0.13 | <0.05 | <0.05 |
| Potassium, mg/L | 91 | 1.6 | 3.2 | 2.0 | 0.39 | 0.08 | 1.96 |
| Magnesium, mg/L | 91 | 6.0 | 12.8 | 8.1 | 1.7 | 0.36 | 8.05 |
| Manganese, mg/L | 87 | <0.01 | 0.03 | <0.01 | 0.02 | 0.17 | <0.01 |
| Sodium, mg/L | 91 | 3.8 | 53.9 | 15.7 | 7.4 | 1.6 | 14.0 |
| Zinc, mg/L | 89 | <0.01 | 0.07 | <0.01 | 0.03 | 0.01 | <0.01 |
| Alkalinity, mg $CaCO_3$/L | 92 | 21.7 | 52.2 | 34.9 | 6.4 | 1.3 | 33.9 |
| Sulfate, mg $SO_4$/L | 92 | 52.8 | 108.9 | 68.2 | 10.7 | 10.7 | 66.2 |
| Chloride, mg/L | 82 | 21.4 | 46.0 | 29.6 | 5.6 | 5.6 | 28.0 |
| Silica, mg $SiO_2$/L | 88 | 4.3 | 7.7 | 6.0 | 0.73 | 0.73 | 6.1 |
| Nitrate, mg N/L | 70 | <0.02 | 2.0 | 1.1 | 0.30 | 0.30 | 1.2 |
| Ammonia, mg N/L | 83 | <0.03 | <0.03 | <0.03 | 0.11 | 0.11 | <0.03 |
| Orthophosphate, mg $PO_4$/L | 76 | <0.02 | 0.31 | 0.02 | 0.05 | 0.05 | <0.02 |
| Dissolved oxygen, mg/L | 41 | 6.0 | 10.2 | 8.9 | 0.72 | 0.72 | 9.0 |
| Total inorganic carbon, mg C/L | 23 | 10.9 | 14.1 | 12.5 | 1.21 | 1.21 | 12.4 |
| Free chlorine, mg $Cl_2$/L | 92 | 1.0 | 2.2 | 1.4 | 0.28 | 0.28 | 1.3 |
| pH, pH units | 93 | 6.9 | 7.1 | 7.0 | 0.05 | 0.05 | 7.0 |

*na = not analyzed

Run #3

| Analyte | N | Min | Max | Mean | Std. Dev. | 95% CI | Median |
|---|---|---|---|---|---|---|---|
| Lead, µg/L | 66 | <0.002 | 2.0 | 0.29 | 0.49 | 0.12 | 0.10 |
| Calcium, mg/L | 63 | 34.5 | 44.5 | 40.0 | 2.6 | 0.65 | 40.3 |
| Copper, mg/L | 61 | <0.003 | 0.02 | 0.003 | 0.01 | <0.03 | <0.003 |
| Iron, mg/L | 64 | <0.002 | 0.17 | 0.01 | 0.03 | 0.01 | 0.01 |
| Potassium, mg/L | 64 | <2.00 | 3.4 | 3.0 | 0.42 | 0.11 | 3.1 |
| Magnesium, mg/L | 64 | <0.025 | 11.1 | 9.7 | 1.4 | 0.36 | 9.9 |
| Manganese, mg/L | 61 | <0.0004 | 0.01 | <0.0004 | <0.0004 | <0.0004 | <0.0004 |
| Sodium, mg/L | 64 | 16.3 | 26.2 | 21.3 | 1.1 | 1.1 | 22.8 |
| Zinc, mg/L | 61 | <0.001 | 0.01 | <0.001 | <0.001 | <0.01 | <0.001 |
| Alkalinity, mg $CaCO_3$/L | 58 | 43.1 | 58.4 | 52.2 | 3.0 | 0.79 | 52.6 |
| Sulfate, mg $SO_4$/L | 56 | 64.6 | 93.6 | 78.6 | 7.5 | 2.0 | 78.8 |
| Chloride, mg/L | 59 | 0.04 | 36.5 | 30.8 | 5.0 | 1.3 | 31.7 |
| Silica, mg $SiO_2$/L | 63 | 3.7 | 8.5 | 6.1 | 1.1 | 0.28 | 5.6 |
| Nitrate, mg N/L | 43 | <0.02 | 1.1 | 0.85 | 0.33 | 0.10 | 0.96 |
| Ammonia, mg N/L | 57 | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 |
| Orthophosphate, mg $PO_4$/L | 57 | 2.5 | 3.3 | 2.8 | 0.16 | 1.3 | 2.8 |
| Dissolved oxygen, mg/L | 51 | 5.5 | 10.8 | 8.7 | 0.76 | 0.21 | 8.8 |
| Total inorganic carbon, mg C/L | 30 | 11.2 | 14.8 | 13.7 | 0.76 | 0.28 | 13.7 |
| Free chlorine, mg $Cl_2$/L | 68 | 0.69 | 2.3 | 1.4 | 0.49 | 0.12 | 1.2 |
| pH, pH units | 68 | 7.4 | 7.6 | 7.5 | 0.05 | 0.01 | 7.5 |

*na = not analyzed

Run #4

| Analyte | N | Min | Max | Mean | Std. Dev. | 95% CI | Median |
|---|---|---|---|---|---|---|---|
| Lead, µg/L | 54 | <0.002 | 1.3 | 0.13 | 0.40 | 0.00 | 0.10 |
| Calcium, mg/L | 59 | 27.7 | 39.6 | 34.3 | 3.0 | 0.93 | 34.7 |
| Copper, mg/L | 59 | <0.003 | 0.22 | 0.005 | 0.03 | 0.008 | <0.003 |
| Iron, mg/L | 60 | <0.002 | 0.03 | 0.01 | 0.01 | 0.003 | 0.004 |
| Potassium, mg/L | 58 | 1.6 | 2.4 | 2.1 | 0.25 | 0.08 | 2.1 |
| Magnesium, mg/L | 58 | 7.1 | 10.7 | 9.0 | 0.91 | 0.36 | 9.0 |
| Manganese, mg/L | 56 | <0.0004 | 0.01 | <0.0004 | <0.0004 | <0.0004 | <0.0004 |
| Sodium, mg/L | 58 | 8.8 | 19.8 | 13.8 | 2.5 | 0.77 | 13.3 |
| Zinc, mg/L | 60 | <0.001 | 0.01 | 0.003 | 0.006 | 0.008 | <0.001 |
| Alkalinity, mg $CaCO_3$/L | 60 | 32.1 | 56.2 | 45.6 | 6.7 | 1.9 | 44.9 |
| Sulfate, mg $SO_4$/L | 59 | 54.1 | 79.6 | 67.3 | 5.8 | 2.6 | 67.1 |
| Chloride, mg/L | 60 | 15.0 | 28.3 | 21.1 | 4.1 | 1.1 | 22.2 |
| Silica, mg $SiO_2$/L | 59 | 4.6 | 10.2 | 6.5 | 0.10 | 0.40 | 6.7 |
| Nitrate, mg N/L | 59 | 0.79 | 1.8 | 1.16 | 0.29 | 0.08 | 1.0 |
| Ammonia, mg N/L | 40 | <0.03 | 0.09 | <0.03 | 0.03 | <0.03 | <0.03 |
| Orthophosphate, mg $PO_4$/L | 59 | 0.30 | 0.54 | 0.46 | 0.05 | <0.02 | 0.47 |
| Dissolved oxygen, mg/L | na* | na* | na* | na* | na* | na* | na* |
| Total inorganic carbon, mg C/L | 57 | 8.2 | 14.4 | 11.2 | 1.9 | 8.0 | 11.1 |
| Free chlorine, mg $Cl_2$/L | 53 | 0.98 | 1.5 | 1.3 | 0.11 | 1.26 | 1.2 |
| pH, pH units | 53 | 7.4 | 7.7 | 7.5 | 0.07 | 0.07 | 7.5 |

*na = not analyzed

Run #5

| Analyte | N | Min | Max | Mean | Std. Dev. | 95% CI | Median |
|---|---|---|---|---|---|---|---|
| Lead, µg/L | 78 | <0.002 | <0.002 | <0.02 | <0.002 | <0.002 | <0.002 |
| Calcium, mg/L | 81 | 27.7 | 47.4 | 38.9 | 6.5 | 1.4 | 42.5 |
| Copper, mg/L | 80 | <0.003 | 0.01 | 0.004 | <0.003 | <0.003 | <0.003 |
| Iron, mg/L | 81 | <0.002 | 0.05 | 0.01 | 0.007 | <0.002 | 0.01 |
| Potassium, mg/L | 54 | 1.0 | 6.1 | 3.9 | 0.82 | 0.22 | 3.9 |
| Magnesium, mg/L | 81 | 6.7 | 15.6 | 11.3 | 3.1 | 0.68 | 13.4 |
| Manganese, mg/L | 81 | <0.0004 | <0.004 | <0.0004 | <0.0004 | <0.0004 | <0.0004 |
| Sodium, mg/L | 81 | 9.0 | 43.1 | 25.1 | 10.4 | 2.3 | 29.0 |
| Zinc, mg/L | 81 | 0.01 | 0.02 | 0.01 | 0.03 | <0.001 | 0.01 |
| Alkalinity, mg $CaCO_3$/L | 80 | 17.9 | 94.3 | 57.2 | 22.4 | 5.0 | 63.4 |
| Sulfate, mg $SO_4$/L | 69 | 43.8 | 136.3 | 100.8 | 23.4 | 5.6 | 106.8 |
| Chloride, mg/L | 74 | 24.0 | 49.5 | 35.0 | 5.8 | 52.0 | 35.1 |
| Silica, mg $SiO_2$/L | 61 | 1.3 | 5.8 | 3.0 | 1.6 | 0.35 | 2.8 |
| Nitrate, mg N/L | 34 | 0.69 | 1.5 | 1.05 | 0.23 | 0.08 | 1.1 |
| Ammonia, mg N/L | 76 | <0.03 | <0.03 | <0.03 | <0.03 | 0.06 | <0.03 |
| Orthophosphate, mg $PO_4$/L | 31 | <0.02 | 0.05 | 0.02 | <0.02 | <0.02 | <0.02 |
| Dissolved oxygen, mg/L | 21 | 5.1 | 10.6 | 8.4 | 1.6 | 0.72 | 8.65 |
| Total inorganic carbon, mg C/L | 64 | 13.4 | 23.7 | 17.6 | 3.4 | 31.7 | 16.0 |
| Free chlorine, mg $Cl_2$/L | 72 | 0.68 | 1.4 | 0.94 | 0.15 | 0.04 | 0.92 |
| pH, pH units | 72 | 7.4 | 7.7 | 7.5 | 0.06 | 0.06 | 7.6 |

*na = not analyzed

***Single-Pass Pipe Experiments***

In a different study designed to investigate the effect of chlorine residual and silicate corrosion inhibitors on copper leaching from rigid copper tubing, a test pipe rig was constructed in one of the USEPA AWBERC facility pilot plants. This study will subsequently be referred to as the "Copper Pipe Study." Some data applicable to compare to the predicitions of this cuprosolvency model are available from this previous investigation.

Cincinnati tap water (Miller WTP) was passed through a series of two small cartridge carbon filters to remove chlorine and reduce TOC, and fed into three heavy-duty polyethylene plastic 200-L (53-gal) reservoir tanks with floating lids. Each reservoir tank had appropriate chemicals added manually to adjust the water quality to target values. Test water contained in each reservoir was continuously recirculated by a magnetic drive pump system. All pump components in contact with the water were constructed of nonmetallic materials.

Each reservoir was used as the initial water feed source for a set of triplicate 8-ft (2.4-m) straight lengths of 0.5-in (1.27-cm) ID type M hard-drawn copper pipe. Plumbing connections were made of 0.5-in (1.27-cm) ID Schedule 80 PVC pipe and fittings. Pipe sections were chemically cleaned in the same manner as described previously for the coupons to assure reproducibility of surfaces in contact with the water.

Each single test pipe section of each triplicate set was isolated from the other two by PVC check valves. Plastic sampling taps were installed at the end of each pipe section, and before the check valves. Water was pumped through the pipes by a pressure-actuated pump. For intervals of flushing after different stagnation periods, flow was triggered by a solenoid valve attached to each of the three test systems, controlled by an electro-mechanical pin timer. After the solenoid valves opened, all pipe systems discharged into a common drain.

The normal mode of operation was to collect samples routinely after 8 hours of stagnation. However, the protocol was varied during the course of the experiments to examine copper levels after various standing times, especially in relation to the depletion of free chlorine residual and dissolved oxygen. Approximately 31.5 litres of test water passed through each pipe section per day (8.3 gpd).

Of the several experiments conducted thus far, one is particularly relevant to the issues of this investigation, and will be covered here. The water quality summary for this experiment is summarized in Table 8.

TABLE 8. WATER QUALITY IN THE COPPER PIPE STUDY.

| Analyte | Mean | Std. Dev. |
|---|---|---|
| Lead, mg/L | <0.002 | 0.000 |
| Calcium, mg/L | 36.8 | 1.4 |
| Copper, mg/L | <0.003 | 0.007 |
| Iron, mg/L | 0.003 | 0.010 |
| Potassium, mg/L | 2.8 | 0.3 |
| Magnesium, mg/L | 10.8 | 2.5 |
| Manganese, mg/L | <0.0005 | 0.002 |
| Sodium, mg/L | 21.0 | 3.3 |
| Zinc, mg/L | <0.001 | 0.007 |
| Alkalinity, mg $CaCO_3$/L | 46.4 | 6.3 |
| Sulfate, mg $SO_4$/L | 70.3 | 7.6 |
| Chloride, mg/L | 25.5 | 7.4 |
| Silica, mg $SiO_2$/L | 5.8 | 1.1 |
| Nitrate, mg N/L | 1.1 | 0.2 |
| Ammonia, mg $NH_3$/L | <0.03 | 0.02 |
| Phosphate, mg $PO_4$/L | <0.10 | 0.01 |
| Total inorganic carbon, mg C/L | 10.98 | 1.72 |
| Free chlorine, mg $Cl_2$/L | 0.4 | 0.0 |
| pH, pH units | 7.6 | 0.1 |
| Temperature, degrees Celsius | 25.† | -- |
| Ionic strength (computed) | 0.0050†† | 0.0006 |

† Approximated
†† Computed by WATEQX

### *Recirculation Solubility Experiments*

New experimental systems were designed, constructed and put into operation by DWRD to specifically address the development and confirmation of equilibrium solubility models for copper(II). As of the time of this report, only one experimental run has been completed, and the data analyzed. A set of recirculation experiments was performed to examine the interrelationships of pH and DIC on cuprosolvency under highly-controlled conditions. These systems are patterned after those originally developed for USEPA asbestos-cement pipe studies and some experiments on lead and galvanized pipe corrosion.[16] Several important modifications were made.

The major modification was the replacement of the stainless steel tanks with 200-L (53-gal) heavy duty polyethylene tanks. All parts of the recirculation system connection plumbing were made of PVC plastic or tygon.™ A magnetic drive centrifugal pump continually circulates water through the 4-ft (1.2-m) length of 0.5-in (1.27-cm) ID type M hard-drawn copper piping at a rate of approximately 3785 litres per day (1000 gpd). The pipe sections mounted in the recirculation systems were chemically cleaned before the start of the experimental runs by the same procedure as previously described for the coupons and pipes used in the single-pass pipe loop systems.

Water was synthesized for the first run of these experiments (reported here) by mixing approximately 3 parts of mixed-bed deionized Cincinnati tap water with 1 part of untreated Cincinnati tap water. DIC was adjusted at the beginning of the run with $NaHCO_3$. Precise chlorine residual (redox potential) control was not possible in these systems, but the free chlorine residual was monitored at least two times per week and sodium hypochlorite solution was added as necessary to attempt to maintain a continual chlorine residual of between 0.2 and 0.9 mg $Cl_2$/L. The pH was generally stable, but was adjusted if necessary once per week, when samples were collected for metals and DIC analysis. The pH of the tanks was controlled within ± 0.1 pH of the target value weekly, but was usually within ± 0.05 pH. Some absorption of $CO_2$ from the air occurred in these low-DIC experiments, even with the floating lids. Therefore, the data analysis approach must take this into account.

Complete water analyses were performed on water samples at the beginning, end, and once per month. Filtration through a 0.1 μm polycarbonate filter membrane with all-plastic apparatus was performed once per month. The filtration procedure followed that described previously for lead studies, except the sample volume was reduced to conserve water in each of the tanks.[62] The soluble metal concentrations were statistically indistinguishable from the unfiltered samples, affirming the use of the unfiltered samples for the saturation index calculations for these systems. For clarity, the filtered sample data points are not shown in the figures.

Data from experiments for DIC=5 mg C/L and pH 7, 8 and 9 are reported here. A partial general summary of the background water quality for these three experimental runs is given in Table 9. The concentrations of chloride and sodium increased over time, from the addition of sodium hypochlorite for disinfection, and either HCl or NaOH for pH adjustment.

TABLE 9. WATER QUALITY FOR DIFFERENT RUNS OF RECIRCULATION STUDY

| | Tank 1 | | Tank 2 | | Tank 3 | |
|---|---|---|---|---|---|---|
| Analyte | Mean | Std. Dev. | Mean | Std. Dev. | Mean | Std. Dev. |
| Aluminum, mg/L | 0.02 | 0.03 | 0.03 | 0.03 | 0.06 | 0.10 |
| Lead, mg/L | <0.002 | 0.000 | <0.002 | 0.000 | <0.002 | 0.000 |
| Calcium, mg/L | 12.5 | 0.2 | 12.5 | 0.2 | 11.1 | 0.3 |
| Iron, mg/L | <0.004 | 0.00 | <0.004 | 0.00 | <0.004 | 0.00 |
| Potassium, mg/L | 0.8 | 0.1 | 0.8 | 0.1 | 1.2 | 0.2 |
| Magnesium, mg/L | 3.8 | 0.1 | 3.9 | 0.1 | 3.7 | 0.1 |
| Manganese, mg/L | <0.0005 | 0.00 | <0.0005 | 0.00 | <0.0005 | 0.00 |
| Sodium, mg/L | 15.8 | 4.4 | 18.0 | 5.2 | 19.7 | 3.8 |
| Zinc, mg/L | 0.01 | 0.00 | 0.01 | 0.00 | <0.001 | 0.00 |
| Sulfate, mg $SO_4$/L | 32.6 | 1.1 | 33.5 | 0.1 | 30.7 | 1.1 |
| Chloride, mg/L | 20.0 | 5.4 | 20.1 | 6.4 | 17.7 | 5.6 |
| Silica, mg $SiO_2$/L | 0.8 | 0.1 | 0.8 | 0.0 | 0.7 | 0.1 |
| Nitrate, mg N/L | 0.3 | 0.0 | 0.4 | 0.0 | 0.3 | 0.0 |
| Ammonia, mg $NH_3$/L | <0.03 | 0.02 | <0.03 | 0.00 | <0.03 | 0.01 |
| Phosphate, mg $PO_4$/L | <0.10 | 0.00 | <0.10 | 0.00 | <0.10 | 0.00 |
| Total inorganic carbon, mg C/L | 5.1 | 0.5 | 5.2 | 0.3 | 5.3 | 0.3 |
| Free chlorine, mg $Cl_2$/L | 0.6 | 0.3 | 0.5 | 0.3 | 0.3 | 0.1 |
| pH, pH units | 7.1 | 0.1 | 8.0 | 0.1 | 9.0 | 0.0 |
| Temperature, degrees Celsius | 25.6 | 1.1 | 25.7 | 1.2 | 24.8 | 0.7 |
| Ionic strength (computed) | 0.0024 | 0.0002 | 0.0025 | 0.0002 | 0.0024 | 0.0001 |

## Data Analysis Approaches

Experimental data has been analyzed in several ways to try to identify factors controlling the equilibrium solubility of copper in the experimental systems. As pointed out by Williams, secondary minerals formed by exposure to natural water systems, such as in oxidation zones around ore deposits, marine corrosion products, and archaeological artifact corrosion products, may serve as "metal ion buffers" that control concentrations in the water.[116] Frequently, these secondary minerals are oxide, hydroxide, hydroxy-sulfate, hydroxy-carbonate, or hydroxy-chloride compounds. These kinds of natural environments are similar in many respects to the conditions of exposure of plumbing materials in drinking water systems. Hence, many computational tools and approaches used by geochemists to investigate natural processes involved in governing metal levels are also highly applicable to corrosion research. Various applications of geochemical modeling programs, and some constraints on their use have been reviewed by Basset and Melchior.[117] Similar application of a geochemical modeling program based on the original WATEQ and WATEQ2 codes to investigate lead corrosion was previously described.[62]

The concentrations of all possible detectable background water constituents cannot be precisely controlled at all times to desired levels in the different types of corrosion and metal leaching experiments used in the DWRD program. Therefore, the data analysis approach to test for solubility controls on copper levels must be robust enough to compensate for this experimental difficulty, and for differences in several constituents from experiment to experiment. Therefore, in addition to graphical analysis, complete background water chemistry information was combined with copper and other metal leaching data and was evaluated with a modified version of the computerized equilibrium aqueous speciation model WATEQX.[112] Modifications by the authors to WATEQX included expansion of the size of the aqueous and solid species arrays to accommodate copper, lead and zinc species of interest in USEPA corrosion research studies.

The first step in employing WATEQX for the data analysis was the adjustment of the thermodynamic data base to be consistent with the best known set of aqueous species, solid species, and their equilibrium constants to characterize the system under study. A critically-reviewed set of equilibrium constants and temperature functions for major potable water constituents has been published by Nordstrom, *et. al.*[118], among others. Other selections of species and equilibrium constants used in WATEQX are given in Table 2.

The WATEQX program was used to compute the ionic strength of the solutions, to derive the DIC concentration from titrimetric alkalinity determinations (carbonic acid equivalence point) and pH as a check, and to provide calculations of the aqueous speciation of the various metals, ligands, and other constituents in the test waters. Correction is made by the program for non-carbonate contributions to alkalinity, such as $HPO_4^{2-}$ and $NH_3(aq)$.[14,30,31,110]

The computer program was also used to determine the ion activity products and saturation states for various solids of interest[14,15,31,62,117]. For example, for the pure $Cu_2(OH)_2CO_3$ (malachite) dissolution reaction given in Equation (29), the activity product ($IAP_{mal}$) expression is defined as:

$$IAP_{mal} = \frac{\gamma^2_{Cu^{2+}}\left[Cu^{2+}\right]^2 \gamma_{CO_3^{2-}}\left[CO_3^{2-}\right]}{\gamma^2_{H^+}\left[H^+\right]^2} \tag{37}$$

where $\gamma_i$ ( gamma) represents the activity coefficient for ion i (i=$Cu^{2+}$, $CO_3^{2+}$, or $H^+$) and the paired brackets $[\,]_i$ represent the mol/L concentration for ion i. The assumption is made that the activity of water and of the pure solid is unity. At equilibrium, the ion activity product of any solid s ($IAP_s$) is equal to the solubility constant $K_{s0}$ for the reaction written exactly the same way as the IAP expression. Therefore, a measure of the saturation state of any solid s may be defined as the "Saturation Index," or

$$SI_s = \log_{10}\left[\frac{IAP_s}{K_{s0}}\right] \tag{38}$$

where equilibrium is indicated by a value for $SI_s$ of 0. Thus, if $SI_s > 0$, the solution is in an oversaturated state with respect to that solid, so a tendency toward precipitation to re-establish equilibrium is indicated. Conversely, if $SI_s < 0$, a tendency toward dissolution is indicated.

Plummer has described the use of the Saturation Index to attempt to identify mineral equilibrium processes controlling the concentration of several metals in ground water systems[119]. In the context of these recirculation solubility, pipe, and coupon tests, the values for SI should approach (but not exceed) zero from the negative direction. Systematic positive values for SI beyond those attributable to analytical imprecision or error may indicate: possible errors in one or more equilibrium constants for copper species; very slow precipitation kinetics of passivating films on the pipe; the formation of mixed solids of higher solubility than pure solids; or complexing species omitted from the aqueous model that enhance metal solubility.

An example of the use of the SI to follow a water chemistry process is as follows. Suppose a water is supersaturated with a solid, such as calcium carbonate in water leaving a lime softening plant. The SI value for that solid will start out at some positive value dictated by the water chemistry at the end of the process, and will then decrease toward zero as precipitation takes place. Because there is some ambiguity to the interpretation of the Saturation Index in some systems, mineralogic observations such as X-Ray, petrographic or chemical scale analysis and the use of mass-balance computations are necessary to corroborate hypothesized chemical processes and solid phases.[119]

A particular advantage of the Saturation Index approach is that it is most sensitive to only a small number of analytes, plus the accuracy of the equilibrium constants. Emphasis can then be applied to optimizing analytical precision and accuracy of those particular analytes, and in their experiemental control. For example, the only direct variables involved in computing SI for the copper hydroxide and hydroxycarbonate minerals are pH, copper, and carbonate ion. Imprecision in the estimation of SI results from the analytical uncertainties in determining pH, DIC, and copper and with the uncertainty associated with the solubility constant $K_{s0}$. For many corrosion systems, the uncertainties in $K_{s0}$ and errors in pH are the largest sources of error in the SI calculations. Additional uncertainty in interpretaion of the computed SI is caused by kinetic restraints governing whether or not a solid dissolves or precipitates, solid impurities, coprecipitation, crystal poisoning, or the interaction of complexes not included in the computation of $IAP_s$. The effects of ionic strength and competitive complexation of other metals and ligands are secondary, and of small magnitude. Therefore, the SI approach automatically compensates for changes in sodium or chloride concentrations, for example, as occur in the recirculation solubility experiments, or small weekly differences in pH or DIC. The approach similarly compensates for variations in calcium concentration, sulfate concentration, pH or other variables from tank filling to tank filling in the other experiments cited in this report.

After the speciation and SI calculations were performed, special FORTRAN programs were written to extract saturation indices and other specific information from the WATEQX output, and reformat it for graphical analysis by other software.

# Experimental Results

## Oxidation Rates and Stagnation Curve Behavior

Because of the observations in the European studies of copper levels that reached maxima and then decreased upon further standing, a detailed investigation was deemed necessary. The reported behavior was in contrast reported the experience with lead pipe, where stagnation curves were usually found to be explained by a model that assumed lead levels were controlled by radial diffusion up to the point of saturation with a passivating solid[16,35]. Also, examination of data collected from the EPA coupon study indicated that copper levels in samples standing over weekends for 72 hours were systematically higher than those taken after 24 hours.

During initial experiments with the copper pipe loop study, chlorine residuals (Table 7) were found to deplete in a matter of hours. As the experiment continued for several months, the rate of chlorine depletion became lessened. After approximately 250 days of operation, the triplicate copper pipe loops receiving the pH-adjusted Cincinnati tap water were sampled at different stagnation intervals over several weeks to determine an empirical stagnation curve. Free chlorine residual and dissolved oxygen concentrations were monitored, in addition to copper concentration. Insufficient sample volume was available to analyze pH.

Figure 15 illustrates changes in the concentrations of copper, free chlorine residual, and dissolved oxygen (DO) for a series of stagnation experiments. Because the starting concentrations of DO and chlorine residual were not always the same, their decreases are expressed as a percentage of the original feed water concentrations. Although chlorine was greatly consumed by reaction with the piping, some was still present up to at least 72 hours. The DO data indicates that, as expected, the stronger oxidant (hypochlorous acid and hypochlorite ion) was mostly consumed first, before the oxygen depletion started. The copper concentrations did not essentially stabilize until after at least 48 hours.

Computations of the Saturation Index for three important copper(II) solids using the WATEQX computer program and complete water chemistry data (see Table 7) are shown in Figure 16. The SI approach was used to compensate for minor differences in water chemistry from one stagnation period to the next. The water is shown to closely approach equilibrium saturation with $Cu(OH)_2(s)$ (cupric hydroxide), *ie.* SI=0, from the undersaturated (negative) side. The calculation assumed the $K_{S0}$ value for reaction (25), representing the cupric hydroxide solid with the high molar surface. Evidence from previous studies argued that it is the likliest form of cupric hydroxide to initially precipitate. The curves for the SI values for CuO(s) (tenorite) and $Cu_2(OH)_2CO_3(s)$ (malachite) are

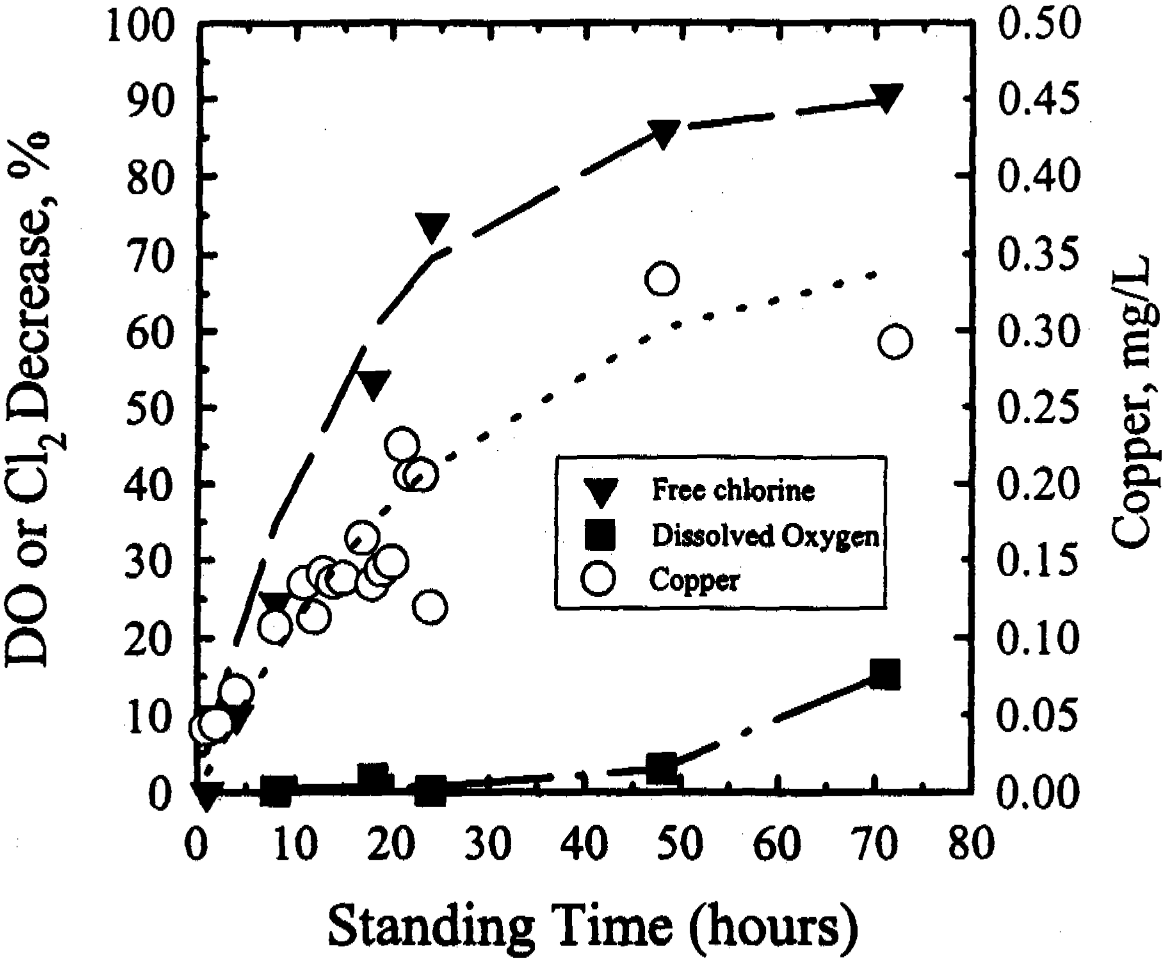


Figure 15. Relationship among depletion percentage for free chlorine residual, dissolved oxygen, and copper concentration over varying stagnation lengths, after 250 days of pipe use.

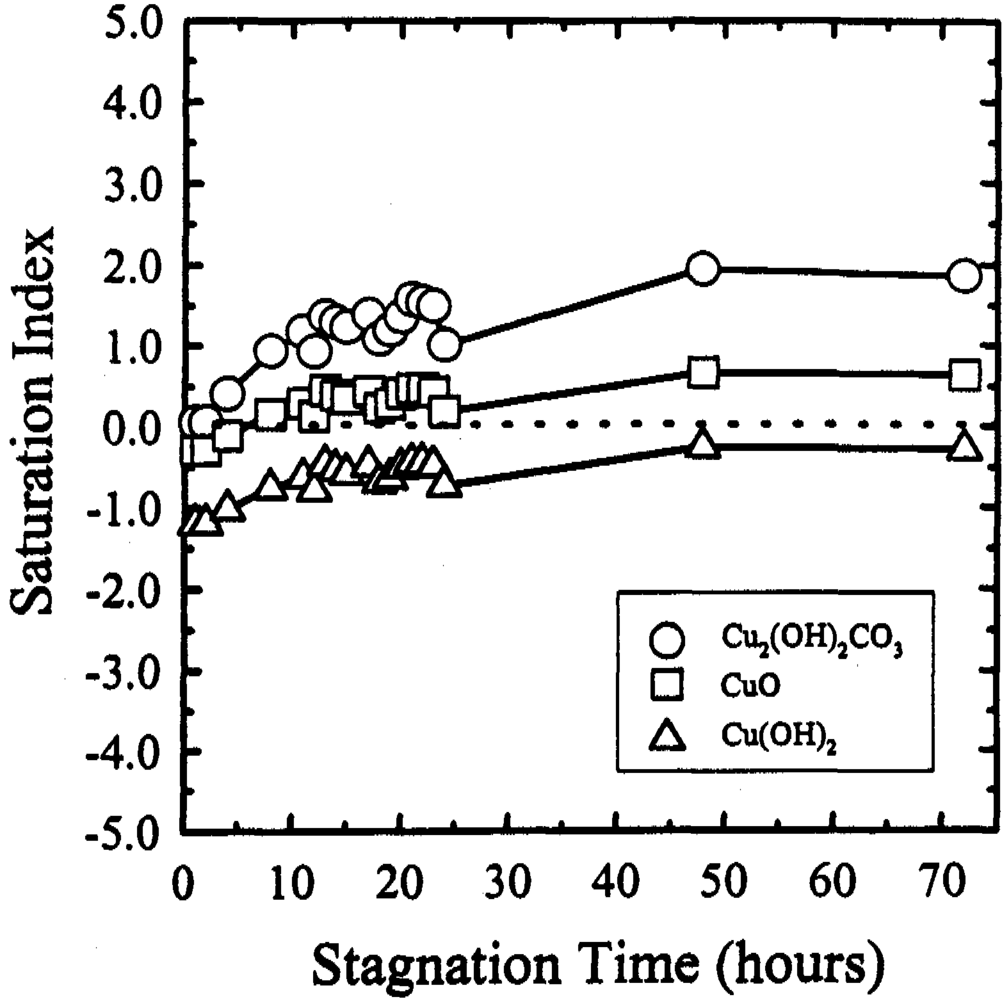


Figure 16. Saturation index changes for three solids during stagnation of different durations in copper pipe loop study. Pipe was aged approximately 250 days

appreciably above equilibrium values, indicating significant thermodynamic supersaturation. Because the copper concentration had essentially stabilized, the calculations are not consistent with the formation of malachite being the mechanism for controlling the copper(II) level in solution in these experiments. Further, precipitation of malachite or tenorite was not indicated by turbid water, erratic copper concentrations indicitive of colloidal dispersion, a dropping SI from positive values toward zero, or by dropping copper levels.

The empirical stagnation curve data was then compared to the predictions of the Kuch and Wagner diffusion model.[35] The maximum copper(II) concentration used as input into the equation was that calculated for the average water quality by the CU2SOL computer program. The empirical and theoretical curves are displayed in Figure 17, with error bars representing standard deviations of replicate samplings. While the theoretical solubility could not be expected to match exactly, the shape of the observed stagnation curve significantly differs from the diffusion-based model. The initial limb of the stagnation curve for the experimental system (over the first 0-2 hr, particularly) is of a much more shallow slope than that produced by the curve representing the assumption of a simple radial diffusion process. This discrepancy indicates that there appears to be a reaction rate-limiting step for copper oxidation, that is not applicable to lead. This limiting step slows the attainment of the equilibrium solubility level. Subsequent examination showed that the internal pipe surface had little surficial film developed on it, but action of an extremely thin and effective diffusion barrier can not be precluded.

There are several important implications concerning cuprosolvency that result from these studies.

- In water supplies maintaining oxidizing disinfectant residuals, copper oxidation and dissolution into the water will take place until that residual is depleted. However, copper levels will stop climbing after saturation equlibrium is reached with a passivating solid (*eg.* $Cu(OH)_2$). If dissolved oxygen is present in addition to the oxidizing disinfectant, continued oxidation and dissolution will take place until the oxygen is then consumed, or passivation occurs.

- The profile of copper concentration versus time in oxidizing systems will depend upon the water chemistry and the relative stabilities of copper(I) and copper(II) aqueous species. The copper concentration in the water may continue to rise for many hours, perhaps substantially beyond the "overnight standing" period normally used for sampling, depending on the operative kinetics in a given system. Complexation of either copper(I), copper(II) or both may be important in these systems.

- In undisinfected water systems having low levels of dissolved oxygen, such as many closed ground water systems, complicated copper versus time profiles may result, as the initial small quantity of oxygen is consumed. This behavior is consistent with the observation of short-term copper concentration maxima, followed by decrease in concentration, reported in several studies.[73,75,76,86,87,120] Copper(I) aqueous chemical speciation and solid reactivity may become extremely important in these systems.

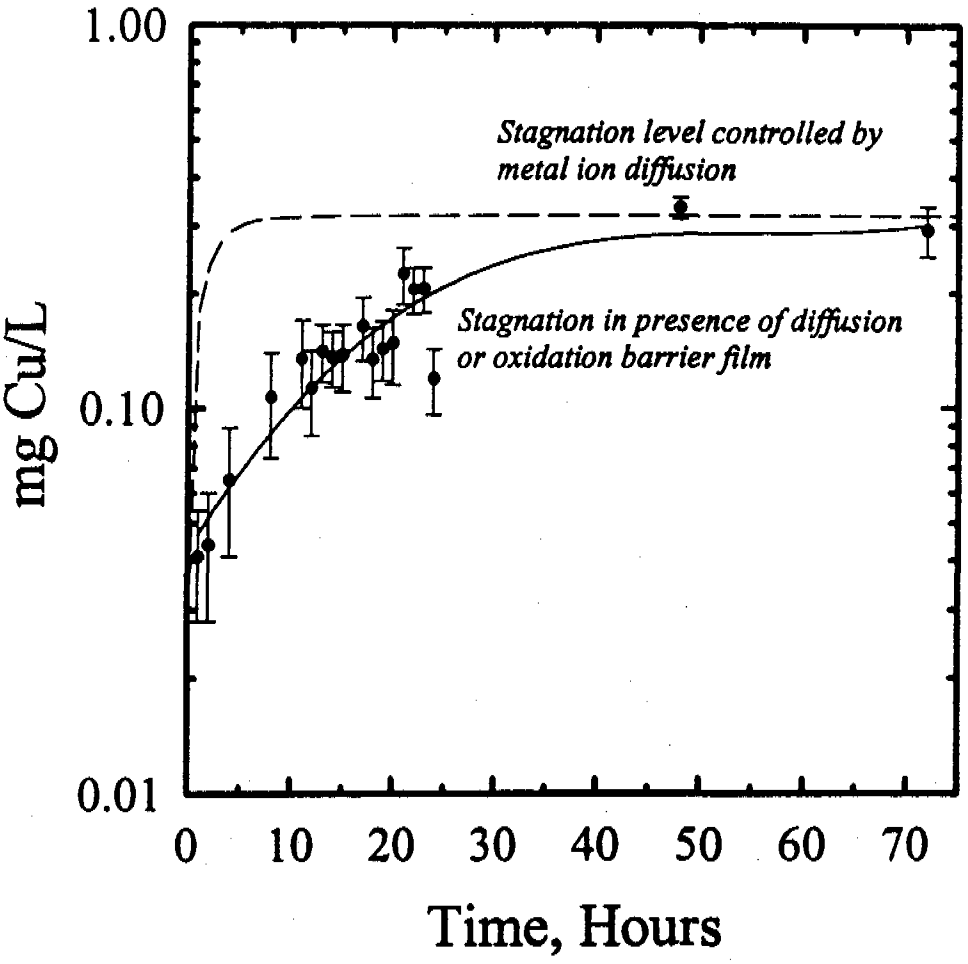


Figure 17. Schematic illustration comparing metal concentrations that would be observed after standing different amounts of time given different controlling chemistry factors.

- Different parts of a distribution system, particularly ones fed by a combination of different water sources (such as wells and conventionally-treated surface water), may exhibit different stagnation profiles.
- Significant variability in copper levels from site to site in the same water system will likely be found in water after the normal number of hours of stagnation found in most sampling programs. This results from the interaction of aqueous complexation and oxidation chemistry of copper, plus effects of the existence or development of passivating films in the pipe.

## The Effect of pH and DIC on Cu(II) Solubility

Although studies are not complete, data collected thus far from some experimental systems can be used to test aspects of the "cupric hydroxide model." Approaching solubility equilibrium from both oversaturation and undersaturation should be a useful tool for examining the validity of the solubility predictions.

Patterson has reported on several studies of the use of the carbonate and hydroxide systems for the removal of copper and other heavy metals from wastewater, which provide a reasonable test for this solubility and speciation model.[121] Precipitation experiments were performed over 24-hour periods at constant pH and DIC. Carbonate concentrations ranged from about 2 mg C/L ($10^{-3.8}$ mol/L) to 8 mg C/L ($10^{-3.2}$ mol/L), over the pH range of 6 to 13. Figure 18a shows the reported precipitation data superimposed on the theoretical solubility curves for the formation of crystalline $CuO(s)$ (tenorite) and $Cu_2(OH)_2CO_3(s)$ (malachite), as would be predicted by the traditional copper modeling approach. For the purposes of the calculations, the ionic strength was assumed to be 0.01, and the temperature to be 25°C. This solubility model condsiderably underestimates the observed copper concentrations throughout the experimental pH range. In contrast, Figure 18b shows the reported precipitation data superimposed on the theoretical solubility curves for the formation of a fresh $Cu(OH)_2(s)$ (cupric hydroxide) precipitate. Except for data at both extremes of DIC in the pH range of 9.5 to 11 where the solubility data is systematically slightly underestimated, the theoretical curves match the data reasonably well. Even over this small range of DIC, the trend of increased solubility with DIC can be discerned in the pH range up to approximately 9.5. The data clearly indicate a higher solubility than would be predicted on the basis of assuming $Cu_2(OH)_2CO_3(s)$ (malachite) formation.

The cause for the discrepancy between pH 9.5 and 11 is not known, and could be caused by either experimental factors or speciation model inaccuracies. Previously, problems with uncertainties surrounding stability constants for a suite of hydroxide, carbonate and hydroxycarbonate complexes for copper(II) were noted, and the discrepancy occurs in the pH range that would be extremely sensitive to such errors, particularly in the formation constants of the complexes $Cu(OH)_2^{\circ}$, $Cu(OH)_3^-$, $CuCO_3OH^-$, and $CuCO_3(OH)_2^{2-}$ which are known to be among the most highly uncertain.

Data from the five experimental runs of the USEPA coupon study can also be the basis for a check on the validity of the cupric hydroxide model. The complete water chemistry analyses (Table

Figure 18a.

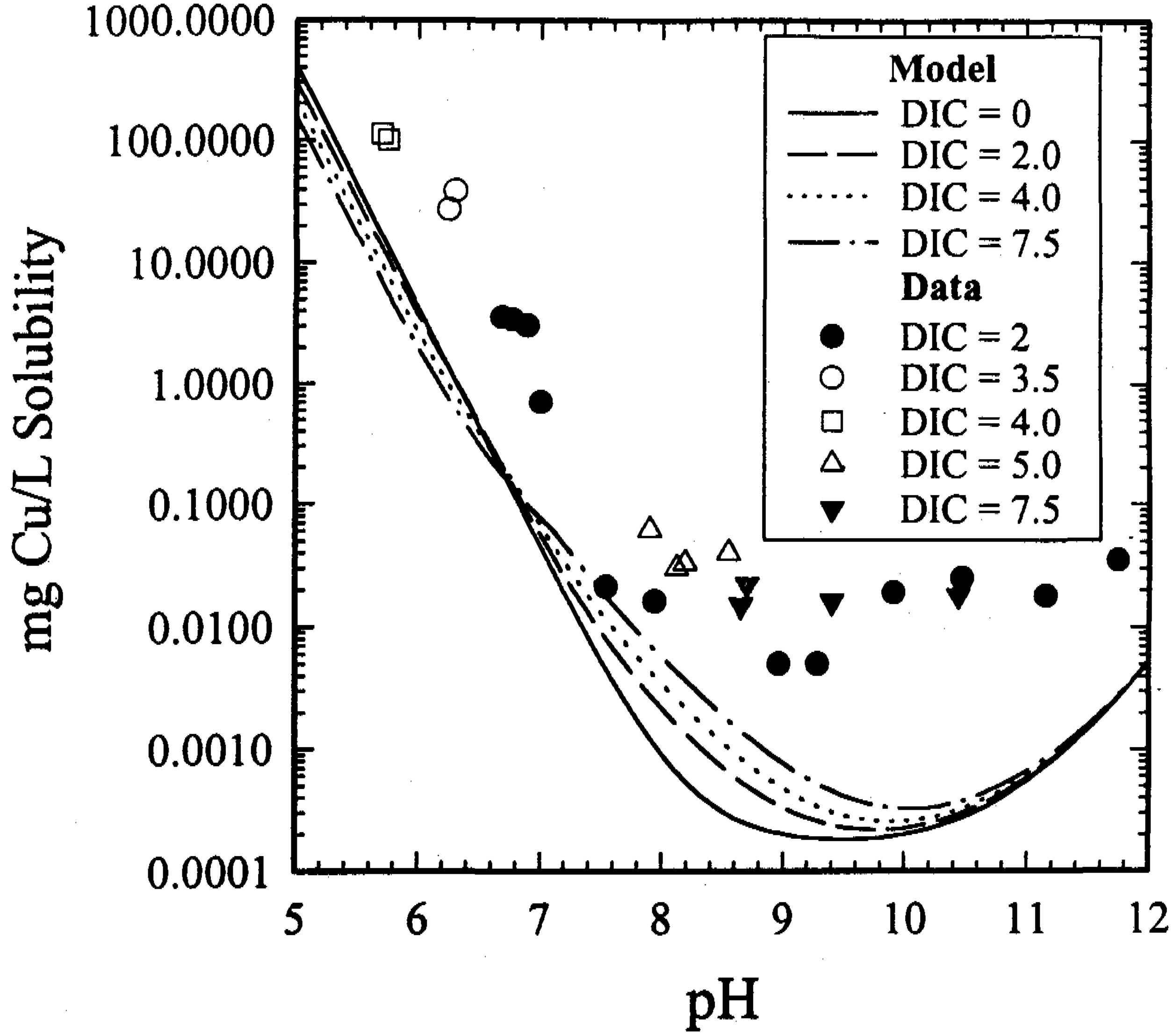
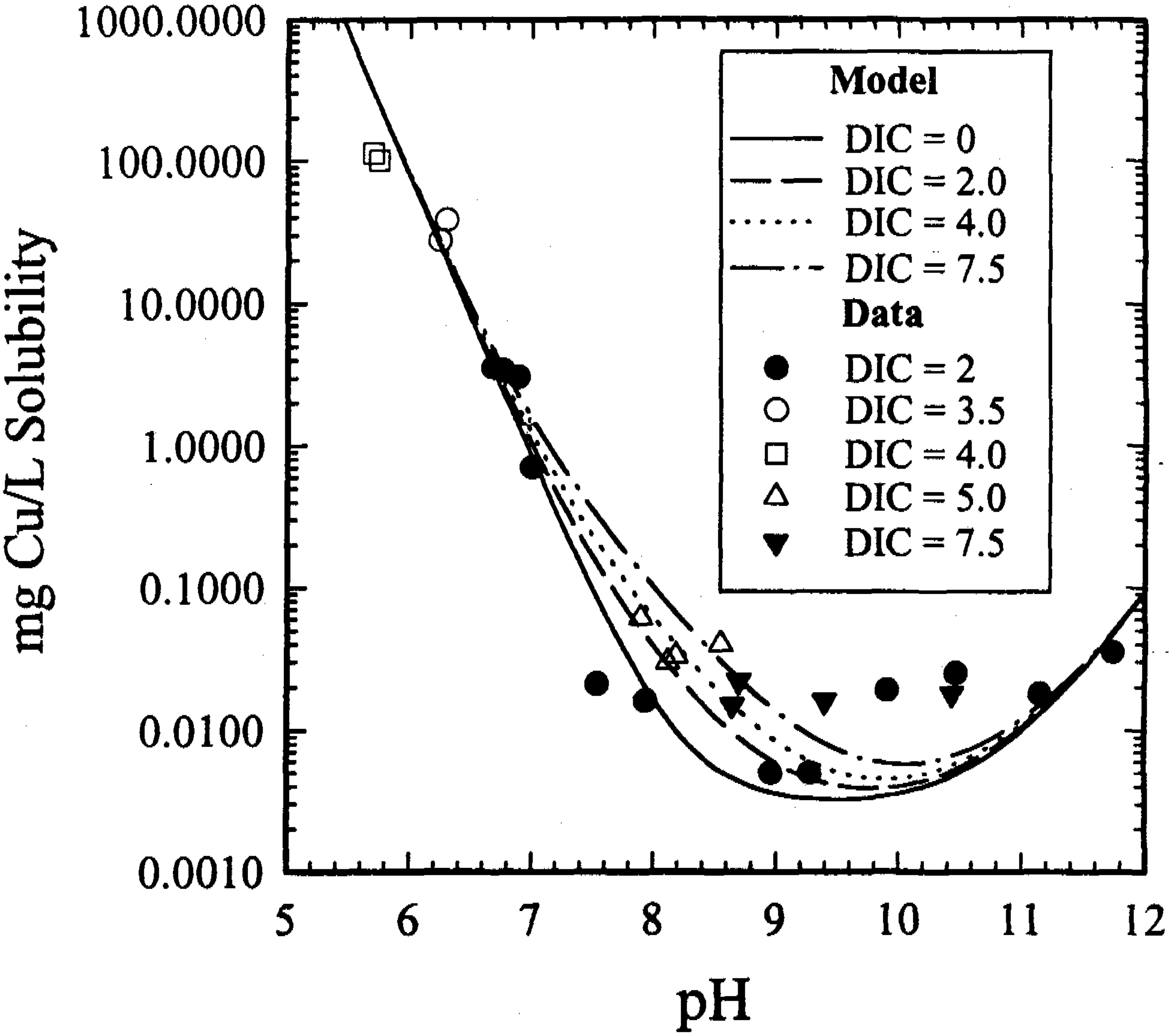


Figure 18. Precipitation date of Patterson (1981) superimposed on two theoretical models for Cu(II) solubility at low DIC concentrations. Models computed for I = 0.01, and 25°C. Controlling solids were assumed to be: a)CuO(s) and $Cu_2(OH)_2CO_3(s)$; b) $Cu(OH)_2(s)$

Figure 18b.


Model
DIC = 0
DIC = 2.0
DIC = 4.0
DIC = 7.5
Data
● DIC = 2
○ DIC = 3.5
□ DIC = 4.0
△ DIC = 5.0
▼ DIC = 7.5
mg Cu/L Solubility
1000.0000
100.0000
10.0000
1.0000
0.1000
0.0100
0.0010
5
6
7
8
9
10
11
12
pH

6) plus copper values from 72-hour standing samples (except Run 3) were used to compute the Saturation Indices for several plausible solids that could conceivably control copper solubility. Again, within the limits of anlaytical and thermodynamic data error, the solid whose Saturation Index is consistently the closest to zero for the long equilibration times of the experiments represents the most plausible candidate for controlling the copper level in the water. The results are summarized in Figures 19a-19e. Because of the small sample volume and handling, pH could not be determined on the stagnation sample, and was assumed to remain unchanged upon standing for the SI calculations. This will introduce some error, but likely not enough to be critical to this exercise. Two of the three experimental runs without orthophosphate addition (Run 2 and Run 5), plus the low level 0.5 mg/L orthophosphate experiment (Run 4) are extremely consistent with the hypothesis of control by $Cu(OH)_2(s)$ (cupric hydroxide), and not at all consistent with control by malachite formation.

The case of the 3 mg/L orthophosphate dosage (Run 3) is somewhat ambiguous with respect to either control by $Cu(OH)_2(s)$ or $Cu_3(PO_4)_2 \cdot 2H_2O(s)$. At the pH of the experiment, which was selected on the basis of exploring lead solubility relationships, there would only be a small difference in copper level if the orthophosphate solid formed instead of the hydroxide. The least-soluble literature solubility constant for $Cu_3(PO_4)_2 \cdot 2H_2O(s)$ was used for the calculation (Table 2), and it is highly uncertain. The data fall virtually midway between literature solubility constant values for $Cu_3(PO_4)_2(s)$ and $Cu_3(PO_4)_2 \cdot 2H_2O(s)$. Therefore, the data are inconsistent with malachite formation, but they do not clearly fit a model based on cuprosolvency control by cupric hydroxide passivation as opposed to cupric orthophosphate passivation. None of the coupons were covered by enough scale to enable good microscopic, elemental or X-Ray diffraction analysis of the films to confirm the proposed mechanisms. A hypothesis of orthophosphate acting as an inhibitor of the copper oxidation rate or as a creator of a thin film possibly of amorphous crystal structure can not be precluded.

The first experiment (Run 1) reflects a large discrepancy with any solubility model based on pH and DIC. The high concentration of sulfate in this system (Table 6) may have provided an unforeseen complication in this study, possibly interfering with the formation of a tight and adhering cupric hydroxide/oxide film[79,122]. Another possible influence is that there was decreased pH buffering in this system relative to the other runs because of the pH being nearer the carbonate system buffer intensity minimum[14,15,30]. A large pH increase resulting from hydroxyl ion production during copper oxidation could put the solution into the field where the model may tend to underestimate the solubility as a result of errors in formation constants or presumed aqueous speciation.

Figure 20 shows the data from the five experimental runs superimposed on a solubility diagram, with curves corresponding to the different average experimental DIC and orthophosphate concentrations. The figure also shows the computed solubility line for one set of $\Delta G_f^\circ$ data for $Cu_4(OH)_6SO_4 \cdot H_2O$, which is in much closer agreement to the observed data for Run 1. Increases in general corrosion rates for copper under oxidizing conditions caused by sulfate ion have been reported,[95,122] but the applicability of those investigations to this system has not been firmly established. As previously noted, Weiser, *et. al.* have reported the precipitation of various mixtures of

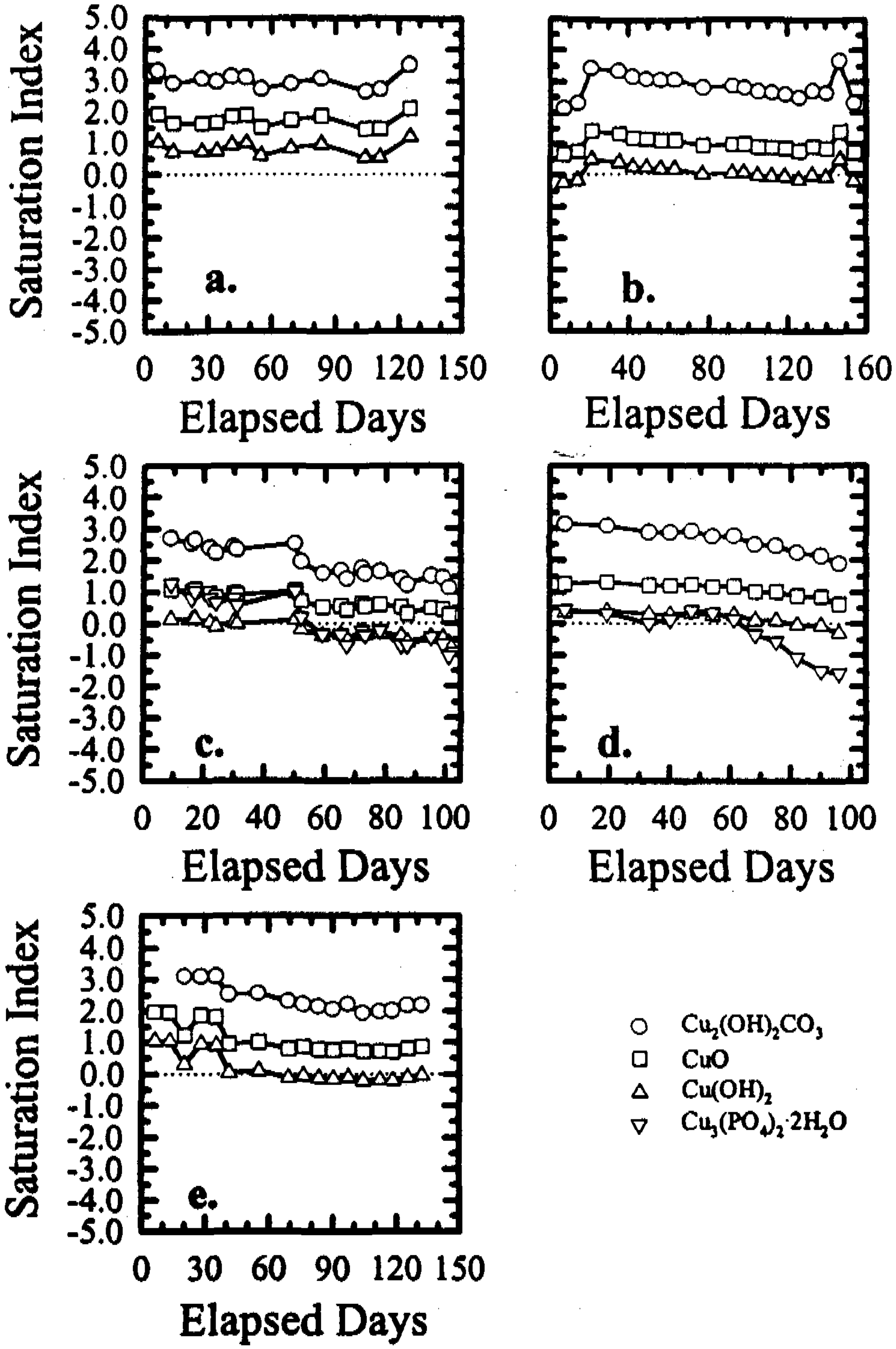


Figure 19. Computed saturation indices for important solids in copper coupon study runs 1-5; a) Run 1, pH = 8.5, 72 hour standing time; b) Run 2, ph 7.0, 72 hour standing time; c) Run 3, pH 7.5, 3 mg $PO_4$/L, 24 hour standing time; d) Run 4, pH 7.5, 0.5 mg $PO_4$/L, 72 hour standing time; e) Run 5, pH 7.5, 72 hour standing time.

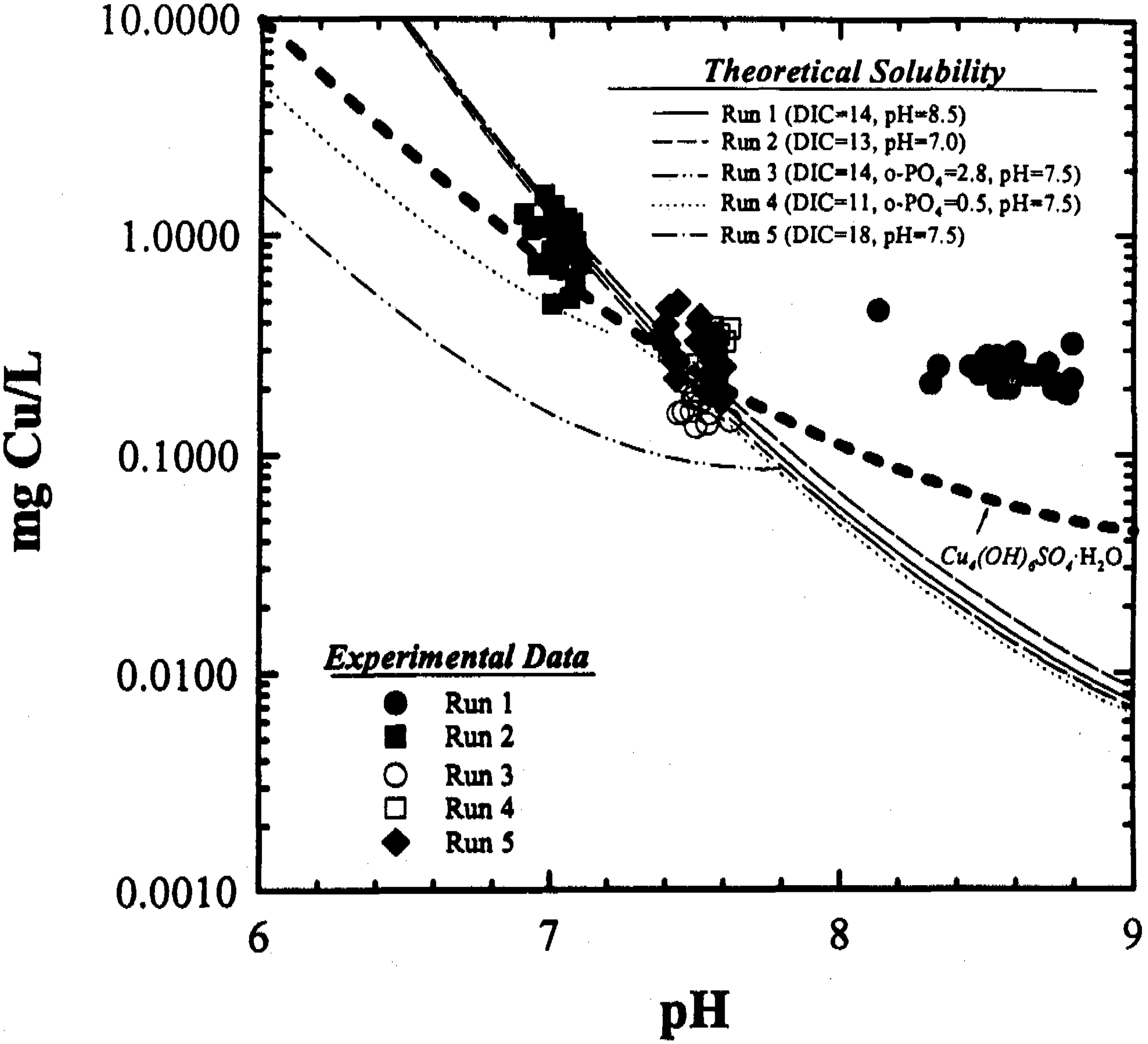


Figure 20. Comparison of theoretical and observed copper levels for coupon study. The wide dashed line indicates the predicted solubility of a hydrated cupric hydroxysulfate in comparison to cupric hydroxide or cupric orthophosphate phases.

cupric hydroxide and a basic cupric sulfate salt in various proportions, depending upon the ratio of cupric sulfate salt to alkali (NaOH) in a solution,[92] and the sulfate term in the empirical equation (27) for copper levels after stagnation from KIWA studies[76] leads to higher copper levels with higher sulfate concentrations. More investigation needs to be done to determine if hydroxide and basic sulfate salt coprecipitation occurs on pipe surfaces, or if cupric oxide or hydroxide formation is inhibited in the presence of high sulfate concentrations, leading to solubility control by copper hydroxy-sulfate minerals.

The most directly-applicable data collected thus far for establishing verification of modeled pH/DIC effects were generated from the USEPA recirculation solubility experiments described above. A background water quality data summary for the experiments with DIC=5 mg C/L at pH 7, 8 and 9 is given in Table 8. Figures 21a-21c show the saturation indices for malachite, tenorite and cupric hydroxide versus time. Clearly, the data for all three systems are much more consistent with copper control by fresh cupric hydroxide, than either $Cu_2(OH)_2CO_3$ (malachite) or CuO (tenorite). Approximately every fourth data collection included metal samples filtered through polycarbonate 0.1 μm filters (datapoints not shown). The soluble metal concentrations were statistically indistinguishable from the unfiltered samples, affirming the use of the unfiltered samples for the Saturation Index calculations for these systems.

Interesting results were obtained from X-Ray diffraction and Energy-Dispersive X-Ray analyses of the deposits formed on these experimental pipes. Consistent with the oxidation multi-layer theory discussed in a previous section, both $Cu_2O(s)$ (cuprite) and broadened peaks corresponding to finely-crystalline or poorly-ordered CuO(s) (tenorite) were found on all pipe specimens in these systems where chlorine residuals were constantly maintained and dissolved oxygen levels were above 6 mg/L. The cuprite layer seemed to be better-developed at pH 9 than at pH 7. At pH 7, a trace of malachite was found, but not on either of the other two pipes. Indeterminable quantities of several other solids were found, however, even in these relatively pristine systems. Significant peaks were found in the pH 8 and pH 9 pipes for posnjakite, $Cu_4(OH)_6SO_4 \cdot H_2O(s)$, even though sulfate levels were only approximately 30 mg/L. This mineral has also been reported in some copper pipes in a German study of pipe corrosion in a hospital.[123] Diffraction peaks likely corresponding to the solid $Cu(Cl,OH)_2 \cdot 2H_2O$ (calumetite) were found, particularly at pH 8 and 7. Qualitative elemental analysis confirmed the presence of S, Cl and also Al on the pipe surfaces. A large peak and a secondary peak apparently consistent with the solid $CuAl_4SO_4(OH)_{12} \cdot 3H_2O$ (chalcoalumite) were found on the pH 7 specimen, but only a corresponding minor peak was found on the pH 8 sample. From the qualitative elemental analysis, the Al concentration on the pipe appeared higher at pH 7, consistent with the general trend in solubility of many aluminum minerals, and a decrease in aluminum in the water during the pH 7 experiment. The presence of aluminum on the pipe is also noteworthy because of the low Al concentration in the water in all three experimental systems, which suggests possiby a strong role for aluminum in the formation of natural diffusion barriers in plumbing and distribution systems.

Some exploratory bench-top experiments were conducted to determine if cupric hydroxide on the pipe surface would be stable enough to be detected by the X-Ray analysis procedure, because

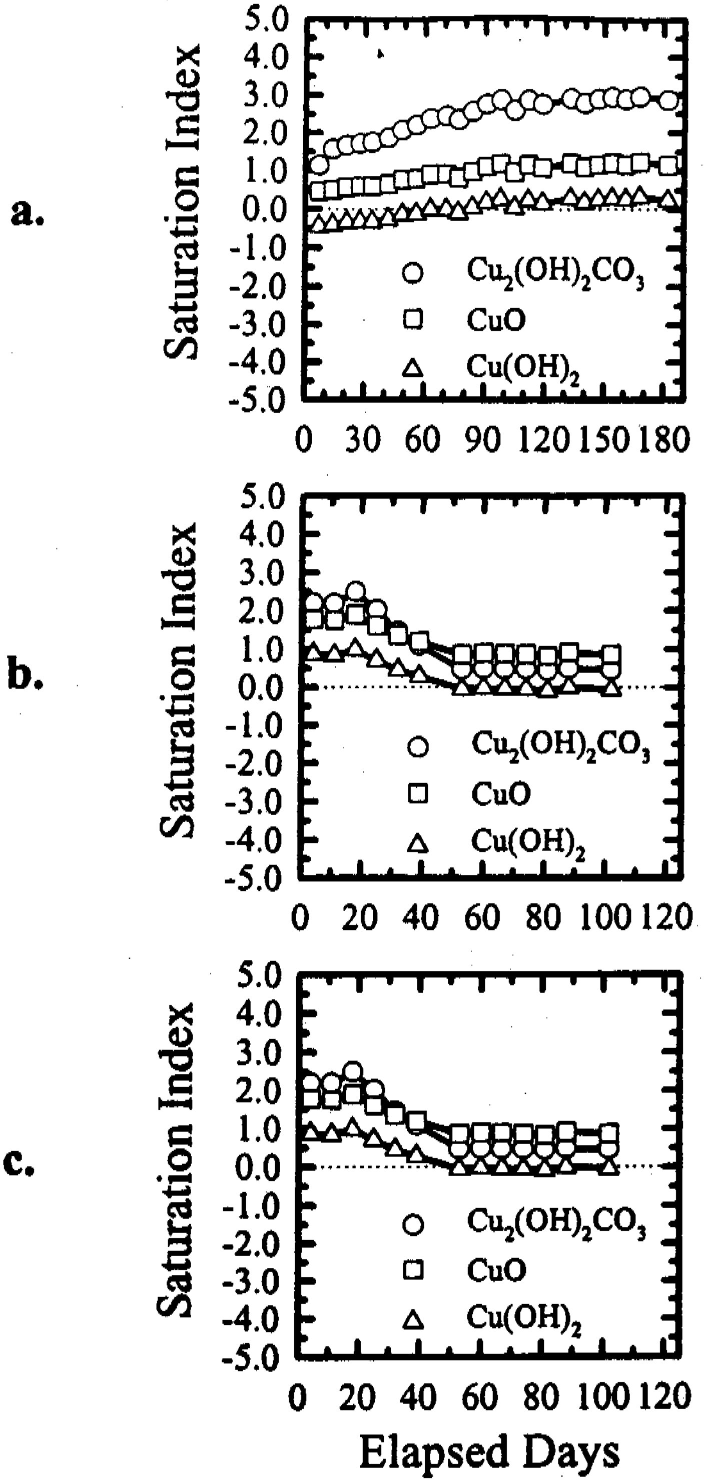


Figure 21. Computed saturation indices for three copper (II) solids in recirculation solubility experiments with DIC=5 mgC/L at: a) pH 7.0; b) pH 8.0; and c) pH 9.0.

none was clearly found on the experimental pipe surfaces (except for the related calumetite). Light blue-green cupric hydroxide was precipitated from sodium hydroxide solution by addition of cupric nitrate solution. The precipitate was removed by filtration, and within several hours of exposure to air, where significant moisture was present on the filter paper, the solid had converted into black cupric oxide with broad diffraction peaks, like that found in the pipe scale samples. These observations agree well with the aging phenomena found in a study of copper precipitation from alkaline solution previously reported.[72] They also show that a similar change in the mineralogy of the pipe deposit would likely occur during the pipe removal, scraping and sample mounting processes. Therefore, the analyses of the pipe samples from these experimental systems are considered to be consistent with the saturation index calculations showing cuprosolvency control by cupric hydroxide.

## The Effect of Aging on Copper Levels in the Water

An implication of considerable importance that results from the cupric hydroxide model is that given identical stagnation times, equivalent water usage patterns, and the absence of unrelated mineral deposition producing diffusion barriers, standing copper levels should decrease over time. The aging process consists of both the recrystallization and dehydration of $Cu(OH)_2(s)$ to $CuO(s)$ described previously,[31,65,66,72] and the slow formation of $Cu_2(OH)_2CO_3(s)$ in the lower pH range below the $CuO(s)$ stability boundary. Wagner has indicated this trend is evident in a German corrosion study published in 1988.[9]

In the United States, most Lead and Copper Rule monitoring programs do not produce samples that represent a broad spectrum of plumbing ages, or samples that are appropriately targeted for the copper pipes. However, a recent study in California conducted by Larry Walker Associates, Inc. for the Contra Costa Central Sanitary District was completed to estimate the impact of residential plumbing as a source of metal contamination of water received by the sewage treatment plants[†]. Approximately sixty homes were sampled in the district, of which approximately thirty residences were fed by water supplied by the Contra Costa Water District (CCWD), and the rest by water produced by the East Bay Municipal Utility District (EBMUD). The residential plumbing systems ranged in age from 1 to 72 years. A summary of general water qualities of the areas sampled is provided in Table 10.

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[†] "Contra Costa Central Sanitary District Residential Metal Study," B. Brandenberg and T. Ross of CCCSD; B. Elzufon, C. Malone and T. Grovhoug of Larry Walker Associates, Inc., Davis, California, engineering study report, July-August 1993.

**TABLE 10. APPROXIMATE WATER QUALITY COVERING SITES IN THE CALIFORNIA WASTEWATER LOADING STUDY.**

| Parameters* | CCWD (Avg.) | EBMUD (mix) |
|---|---|---|
| pH (units) | 8.5 | 8.9 |
| Total Alkalinity (as $CaCO_3$) | 70 | 25 |
| DIC (computed as C) | 17 | 6 |
| Calcium | 16 | 8 |
| Magnesium | 18 | 1 |
| Sodium | 91 | 2 |
| Potassium | - | 10.5 |
| Chloride | 142 | 5 |
| Sulfate | - | 3 |
| Fluoride | 0.93 | 0.9 |
| Nitrate (as N) | - | 0.1 |
| Silica | - | 6 |
| Conductivity (µS) | 731 | 70 |

* mg/L unless noted otherwise

The sampling protocol used was as follows. The tap to be sampled was flushed the night prior to sampling, and the time recorded. In the morning, the resident turned on the tap prior to any other water usage, and discarded the first 500 mL. The next 1000 mL was immediately collected for analysis, so that the copper plumbing was targeted by the sample. The time of this sampling was also recorded. Standing times ranged from 6 to 14 hours, with an average of 7.65. However, 83% of the samples were between 6.2 and 9.1 hours. Because of the observations of slow oxidation and solubilization rates of copper in the EPA studies described in an earlier section, and the nearly linear increase observed repeatedly for the first 10-15 hours in disinfected systems, the copper leaching amounts can be approximately normalized for comparison by dividing each of the concentrations by its standing time to convert them into rates. Figure 22 shows the resulting distribution of copper leaching rates, expressed as micrograms of copper per hour, for the different plumbing ages.

Two aspects of the data distribution are notable, though caution must be exerted to avoid overinterpreting the data because of its limitations and assumptions used. First, based on pH and DIC considerations shown in Table 9, reference to Figure 4 predicts that for fresh copper piping the water from CCWD would be considerably more cuprosolvent at equilibrium than the water from EBMUD, even though neither would really be considered actually corrosive toward copper. This appears to be borne out by the distribution of copper leaching rates, particularly for residences newer than about 20 years old. Second, there is a downward trend in both sets of data, indicating that copper leaching into the water lessens with aging of the piping in the homes, up to some point where the distribution becomes considerably more random. This point appears to occur in the 20-35 year range, but cannot be determined very reliably from this dataset without more stagnation curve profile information to validate the assumptions. For example, there is no direct quantitative predictor of copper leaching rate based on computed equilibrium solubility, and vice versa. If

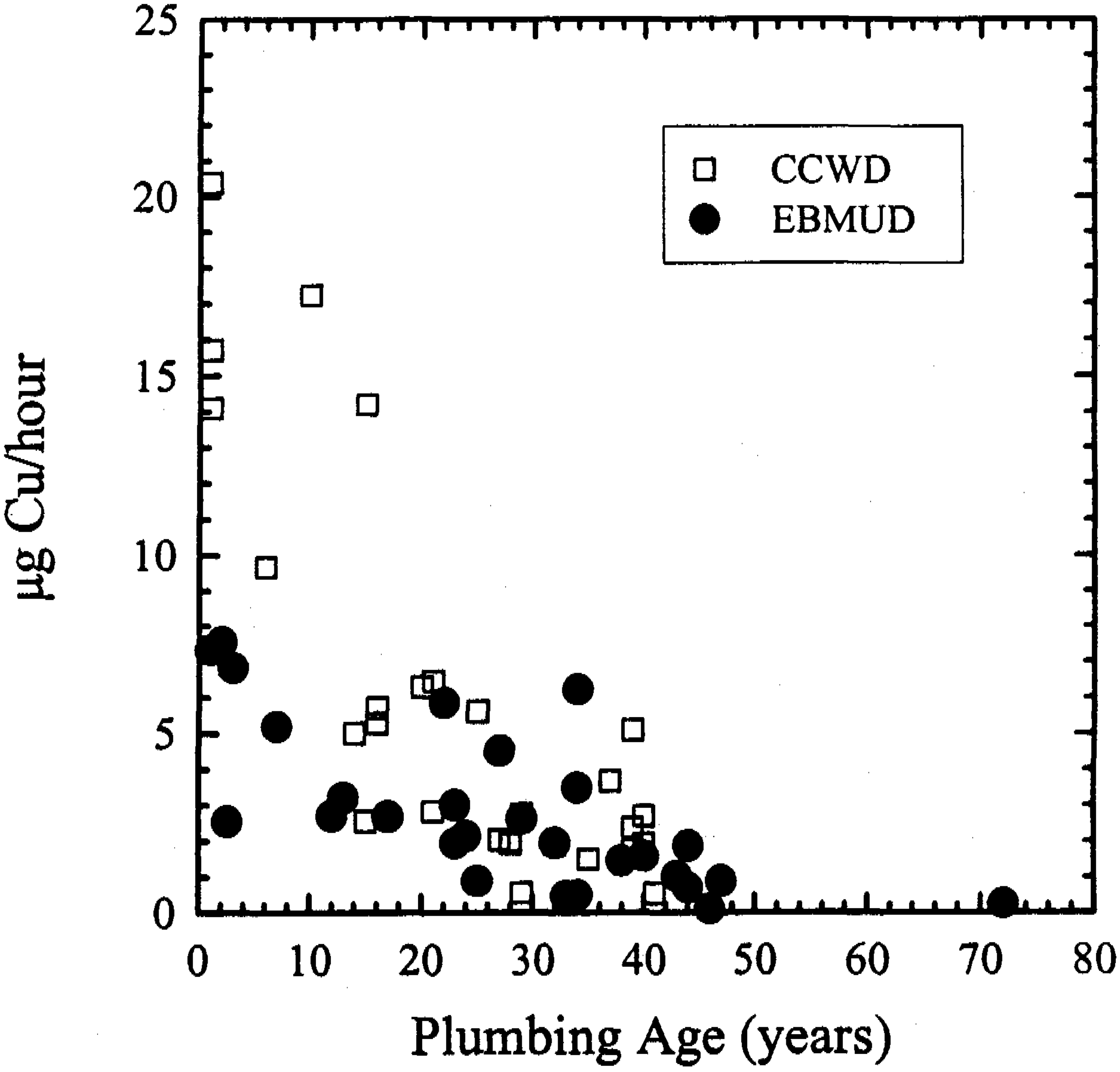

Figure 22. Distribution of adjusted copper leaching rates versus age of plumbing for one litre samples from the residential metals study of the Contra Costa Central Sanitary District.

water in contact with pipe at one or more of these sites reached the equilibrium copper concentration before it was drawn, then dividing the sampled concentration by the standing time will bias the resulting computed rate to be erroneously low. If this phenomenon tended to occur more readily in older pipes with well-developed passivating films of low solubility (such as malachite), the slope of the aging trend would decrease too rapidly.

Although the study data cannot be shown to *prove* the validity of the cupric hydroxide model for young copper plumbing systems, they do indicate behavior that is consistent with assumptions of the model, and logical predictions from it.

# Conclusions

## Significance of pH and DIC in Cuprosolvency Control

This research has shown conclusively that trends in copper concentrations resulting from uniform corrosion are predictable for a range of appropriate water qualities. Given that field conditions frequently do not reflect equilibrium conditions, some discrepancy between the model predictions and the results of normal tap water monitoring programs is understandable. Nonetheless, water quality objectives for copper corrosion control by pH and DIC adjustment can be predicted without the necessity of complicated experimental and field studies, by using the described equilibrium chemistry model.

The relationship between DIC and copper(II) solubility has been shown to be very complex. DIC can play several significant roles as follows, depending upon its concentration, other water chemistry factors, age of plumbing, water flow amount and pattern of use.

- In new plumbing or at high pH, where cupric solubility is controlled by either cupric hydroxide or cupric oxide, DIC complexes dominate copper speciation above approximately pH 6.5, resulting in increased cuprosolvency. The solubility enhancement effect is strongest in the DIC range of 0 to 20 mg C/L, but the predicted soluble copper at equilibrium is still below about 1 mg/L.
- DIC serves to control the buffer intensity in most water systems, therefore, sufficient DIC is necessary to provide a stable pH throughout the distribution system for corrosion control of copper (and lead). In treatment practice, the increase in DIC to ensure pH control through buffering will probably need to be offset by increasing pH to maintain lowered cuprosolvency.
- Possibly offsetting the solubility enhancement of copper(II) by carbonate complexes is the possibility that moderate DIC levels would logically accelerate the formation of passivating $Cu_2(OH)_2CO_3(s)$ (malachite) films in the pH/DIC region where it would be thermodynamically stable. Thus, enhancement of conditions that would hasten the formation of malachite, CuO (tenorite), or both, relative to cupric hydroxide would result in a net lower copper(II) solubility, even with some additional carbonate complexation.

- In the region of pH from approximately 8.5 to 10, this solubility model occasionally systematically predicts slightly lower copper(II) solubility than has actually been observed in some well-controlled pipe loop and precipitation studies. The discrepancies are most likely the result of formation constant errors, inadequacies of understanding copper(II) aqueous complexation with hydroxide and carbonate, or the presence of metastable copper solids associated with anions other than carbonate or hydroxide.

## Significance of pH and Orthophosphate in Cuprosolvency Control

Because cupric hydroxide solubility has been shown to be a better estimate of cuprosolvency tendencies in many water systems than previously presented models based on $Cu_2(OH)_2CO_3$ (malachite) equilibrium, orthophosphate in sufficient dosage is now predicted by the models to have an ability to further reduce copper levels in the pH range of approximately 6.5 to 7. The necessary dosage is hard to quantify, but the calculations suggest that 3-5 mg $PO_4$/L orthoposphate may be necessary to achieve substantial improvements in cuprosolvency over the DIC/pH system at approximately pH 8, but perhaps only 1-3 mg $PO_4$/L at approximately pH 7.

While orthophosphate in sufficient quantity may decrease cupric ion solubility relative to the formation of cupric hydroxide solid, the calculations suggest that for pH above approximately 6.5 the equilibrium solubility of $Cu_2(OH)_2CO_3$ (malachite) is still lower. Therefore, lower solubility levels may ultimately be achieved by aging in the absence of orthophosphate. The interesting experiments of Werner, *et. al.*[86,87] on aged copper pipe possibly suggest a complicated role for orthophosphate. These experiments, though performed in the initial presence of oxygen but in the absence of a chlorine residual, showed that at a high DIC level where formation of malachite would be most likely, higher copper levels are produced by the presence of orthophosphate at pH 7.2. This possibly indicates inhibition of the normal transformation that would take place from cupric hydroxide to malachite with aging. More experimentation with orthophosphate is clearly warranted.

More investigation is also still needed to ascertain objectively and consistently if any synergistic cuprosolvency reduction effect exists from the use of blended phosphates rather than orthophosphate, as has been suggested by one research project.[124]

## Implications for Controlling Highest Copper Exposures

The distinct aging process noted for recrystallization and development of cupric hydroxide, cupric oxide, and cupric orthophosphate films raise an important caution for determining the highest exposures to copper in drinking water. While the Lead and Copper Rule[2] was specifically intended to bias the sampling site selection towards locations with high relative risks for lead exposure, these sites do not generally correspond to commensurately high risks for copper exposure, which include: newest construction and remodeling, areas with unstable pH, and dead ends.

Changes in solubility of copper as pipes age, and films build up, has been indicated in several studies and by practical experience. This investigation has shown how such a phenomenon may have a firm chemical basis that has heretofore been unappreciated. In practice, when attempting to predict the impact of different water treatment scenarios on cuprosolvency, a fruitful strategy may be to apply different solubility models depending on the general age of the plumbing systems involved. For example, for older neighborhoods where $Cu_2(OH)_2CO_3$ (malachite) and CuO (tenorite) have had sufficient time to form an integral part of the passivating film, a better prediction of pH, DIC and orthophosphate dosing impacts would be obtained assuming their presence (ie. Figures 6, 7, 9 and 13b). Conversely, for areas predominantly of new construction, the "cupric hydroxide model" would be more applicable (ie. Figures 3,4,10, and 13a).

Examination of copper concentrations in coupon cells and pipe loop systems after various standing times show that the redox conditions of the water play a crucial role in defining stagnation profiles for copper plumbing. These experiments are complementary to those reported in the European studies, by showing that under oxidizing conditions resulting from both chlorine residuals and the presence of several mg/L of dissolved oxygen, copper concentrations continue to rise to saturation levels of passivating cupric solids. This almost linear increase in concentration frequently extends far beyond the 6-16 hour standing time requirement of regulatory sampling.

## Significance of Cupric Hydroxide Model for Demonstration Studies

Utilities may encounter some complications in projecting pipe loop or coupon leaching cuprosolvency data obtained in demonstration studies to behavior across the whole distribution systems. In the absence of significant concentrations of orthophosphate, this research indicates that for the short timeframes of most experimental studies conducted to satisfy Lead and Copper Rule requirements (6 months to 2 years in most cases), cupric hydroxide will usually be the most important solid phase, rather than CuO(s) (tenorite) or $Cu_2(OH)_2CO_3$(s) (malachite). Both pH and DIC effects will be magnified in the experimental systems, relative to significantly aged piping in the distribution system.

Because of the slow oxidation rate relative to diffusion rates, it is unlikely that copper concentrations are at "equilibrium" when samples are taken from experimental pipe rig systems operated to allow "overnight" standing times, unless the systems have been operated long enough that the passivating films are well-developed, perhaps for years.

When orthophosphate dosing is tested, overestimates of its effectiveness could be obtained for distribution system areas having old copper plumbing with well-developed passivating films. The experimental systems may also be very sensitive to minor dissolved oxygen, chlorine residual, sampling, and stagnation time fluctuations, because of the highly non-equilibrium nature of copper behavior in the 6-16 hour time period.

## Significance of Chlorination and Aeration on Copper Levels

The presence of oxidizing agents appear to increase the rate of copper dissolution, and promote the formation of copper(II) aqueous and solid species, rather than copper(I) species. Confusing data may be obtained from water systems that employ oxidative processes for different reasons. A system never having used aeration or disinfection, that institutes such a process may encounter much higher copper levels than previously, because of the difference in solubility of copper metal or copper(I) as opposed to copper(II) (see Figures 11-13). Sampling of water from copper piping done under nonequilibrium conditions will also likely show fluctions depending on the levels of oxidants in the system.

## Future Research Needs

The absence of fundamental equilibrium constant and solubility constant data for important aqueous species and solids involved in passivation film formation is the most significant constraint on the ability to extend the model predictions in a more quantitative way to systems using corrosion inhibitors, or with significant concentrations of other chemical species (eg. orthophosphate, polyphosphate species, ammonia, natural organic matter, etc.) that would measurably impact cuprosolvency. The reliability of the carbonate and hydroxide complexation predictions are also weakened for pHs above approximately 8.5 because of the lack of adequate equilibrium constants and experimental confirmation. The most comprehensive and reliable research into copper hydrolysis and carbonate complexation has focused on either systems with much higher copper concentrations than drinking water, where many polymeric cationic hydroxide complexes form (eg. $Cu_2(OH)_2^{2+}$, $Cu_3(OH)_4^{2+}$, etc.), or under sea water conditions. The general uniformity of the pH of sea water amongst the major oceans (about 8.0-8.3) and the high salinity make many of these studies too restricted for drinking water application.

To most effectively address the data gaps, and to provide the most useful and practical information to water utilities and consultants investigating cuprosolvency control, future research should depart from the traditional "field study" orientation, and address several critical information needs in the laboratory. These important needs are:

- Analyze pipe deposits from copper plumbing systems of various ages, to determine the pH/DIC and time-dependent stability domains of $Cu(OH)_2$ (cupric hydroxide), CuO (tenorite), and $Cu_2(OH)_2CO_3$ (malachite). Deposits should also be examined to determine the water chemistry domains responsible for forming cupric hydroxysulfate solids, such as $Cu_4SO_4(OH)_6 \cdot H_2O$, which may be much more important in controlling cuprosolvency than has traditionally been suggested. These analyses must include compound specific methodologies, because conventional elemental analysis techniques (such as x-ray fluorescence, energy-dispersive x-ray analysis on an SEM, or ICP analysis of dissolved coatings) can not readily and accurately differentiate among carbonate solids and oxide/hydroxide solids. Such differentiation is critical in understanding the mechanism of passivation, and to developing a quantitative model for cuprosolvency treatment.

- Analyze pipe deposits from copper plumbing systems in utilities using phosphate-containing inhibitors, to determine the copper solids present. This is particularly important for the pH range of approximately 6 to 8. Using this information, the applicability of the existing solubility data for $Cu_3(PO_4)_2 \cdot 2H_2O$ can be assessed, and new solubility experiments can be conducted to obtain the necessary constants and temperature functions for the actual scale minerals found in real systems. Once again, compound-specific analytical techniques are required for this research to be highly useful.

- Determine if a relationship exists between DIC concentration and rate of malachite or tenorite formation in the pH range of 7 to 9, that could be used to accelerate the reduction of cuprosolvency.

- Conduct laboratory experiments to determine for the first time the solubility of important cupric orthophosphate solids that have been found in nature and which may be important in plumbing systems (see Table 5).

- Refine the formation constants for the uncharged and anionic hydrolysis complexes of Cu(II), such as $Cu(OH)_2^{\circ}$, $Cu(OH)_3^-$ or other possible species. Further investigation of the hydrolysis of Cu(I) also appears to be needed. These determinations should to be made at appropriate ionic strengths to enable extrapolation to $I=0$ for modeling, and should encompass the temperature range of 5-55°C.

- Refine the formation constants for copper(II) carbonate and mixed carbonate/hydroxide complexes (eg. $Cu(CO_3)_2^{2-}$, $CuCO_3OH^-$, $CuCO_3(OH)_2^{2-}$) under the same conditions as the hydroxide complex experiments suggested above.

- Investigate the effect of chloride and sulfate on the mineralogy of passivation films formed, and their properties as oxidation barriers.

To gain further understanding of copper chemistry in drinking water and its likely response to various water treatment changes in the future, several other research areas need considerable attention. Some of these areas are:

- Investigate the effect of free ammonia and chloramines on the speciation of the dissolved copper, and the oxidation rate. In conjunction with this activity, analyzing standing water samples for both Cu(I) and Cu(II) would help elucidate the complexation and oxidation chemistry.

- Investigate the characterization of NOM present after typical drinking water treatment and disinfection, and its impact on copper oxidation rates, aqueous speciation and passivation film formation.

- Investigate the relative affinity and conditional stability constants for copper with various polyphosphate species present in formulations used for iron and manganese control, to determine the optimum conditions and mechanisms for the reduction of copper dissolution. Also, investigate a possible pH-dependent tendency of polyphosphate and silicate species to interfere with the formation of normal cuprous and cupric hydroxide/oxide films.

- Investigate the "stagnation curve" behavior of copper in plumbing systems in relation to oxygen and chlorine levels, and different conditions of cumulative water flow and relative flow/stagnation cycling. The impact of these factors on the mineralogy and permeability of passivation films needs to be determined, particularly in relation to the replacement of cupric hydroxide films with malachite.

- The research presented here suggests malachite to be relatively unimportant in controlling copper(II) levels in the short-term (months to years). Therefore, some research in natural water systems may need to be reexamined for the role of basic cupric sulfates or adsorption as significant controls of cupric ion activity under some circumstances, instead of malachite as has often been assumed.

Some of the latter topics are currently under investigation by different research groups. However, the time constraints of drinking water and waste water regulations create a need for more immediate activity and support in these research areas. Research areas beyond those listed here will probably also be found to be important as more studies are done.

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